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2nd USA/USSR Symposium on Physical/Chemical Treatment from Municipal and Industrial Sources Held at the Taft Center, Cincinnati, Ohio on November 12-14, 1975

Environmental Protection Agency, Washington, D.C.

Prepared for

United States-Union of Soviet Socialist Republics Working Group on the Prevention of Water Pollution from Municipal and Industrial Sources

Nov 75

USA-USSR
WORKING GROUP
ON THE PREVENTION OF
WATER POLLUTION
FROM MUNICIPAL AND
INDUSTRIAL SOURCES

NOVEMBER 1975

PB 266 702

USA·USSR

SYMPOSIUM ON
PHYSICAL/CHEMICAL TREATMENT FROM MUNICIPAL AND INDUSTRIAL SOURCES

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The second cooperative USA/USSR symposium on the physical-chemical treatment of waste waters from municipal and industrial sources was held in Cincinnati, Ohio at the Taft Center from November 12 through Novermber 14, 1975.

The sixteen papers that were presented at the symposium (nine US and seven USSR) are reprinted in English in this volume. The two papers presented in Moscow in May of 1975 by the Soviets that were never bound in the previous volume are included as an appendix.

This volume is reprinted in English in accord with the protocol signed by the delegation leaders on November 21, 1975 in Washington, DC

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from
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from
Municipal and Industrial Sources

Taft Center
Cincinnati, Ohio
November 12-14, 1975

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PREFACE

The second cooperative USA/USSR symposium on the physical-chemical treatment of waste waters from municipal and industrial sources was held in Cincinnati, Ohio at the Taft Center from November 12 through November 14, 1975. This symposium was conducted in accord with the protocol of the Fourth Session of the Joint USA/USSR Commission held in Washington, D.C. from October 28-31, 1975.

This symposium was sponsored under the auspices of the Working Group on the Prevention of Water Pollution from Municipal and Industrial Sources. The United States delegation was headed by Harold P. Cahill of the United States Environmental Protection Agency and the Soviet delegation was headed by R. F. Slavolyubov of the Department of Gosstroi in the Soviet Union.

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USA-USSR SYMPOSIUM ON PHYSICAL/CHEMICAL TREATMENT FROM MUNICIPAL AND INDUSTRIAL SOURCES

ADDENDA

Figures omitted from the text are attached. They are:

Page 4, Figures 1 and 2.
Page 8, Figure 6.
Page 9, Figure 7.
Page 16, Figure 1.
Page 17, Figures 2 and 3.
Page 20, Figure 1.
Page 21, Figure 2.
Page 24, Figure 5.
Page 25, Figure 6.

PREFACE

The second cooperative USA/USSR symposium on the physical-chemical treatment of waste waters from municipal and industrial sources was held in Cincinnati, Ohio at the Taft Center from November 12 through November 14, 1975. This symposium was conducted in accord with the protocol of the Fourth Session of the Joint USA/USSR Commission held in Washington, D.C. from October 28-31, 1975.

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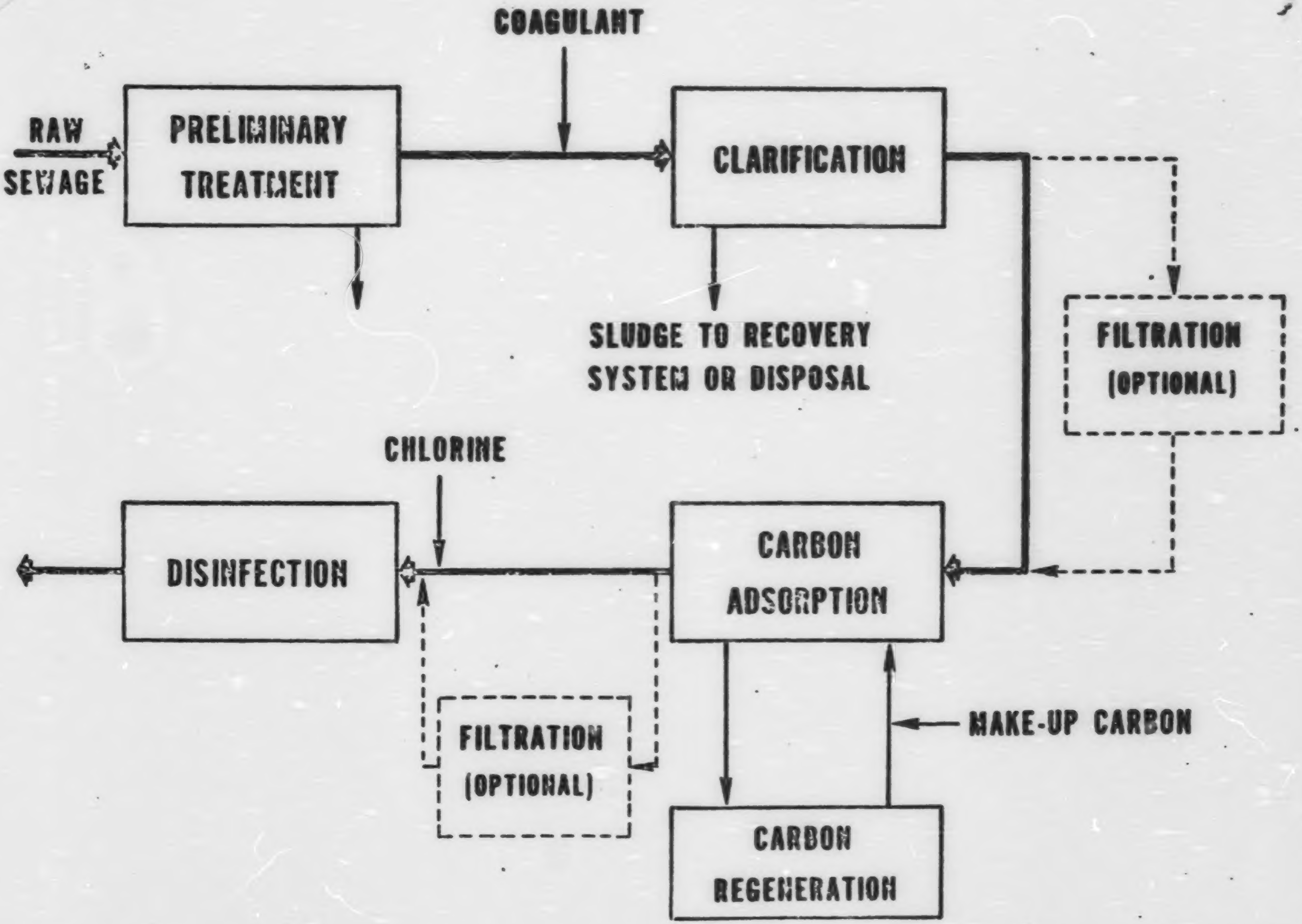
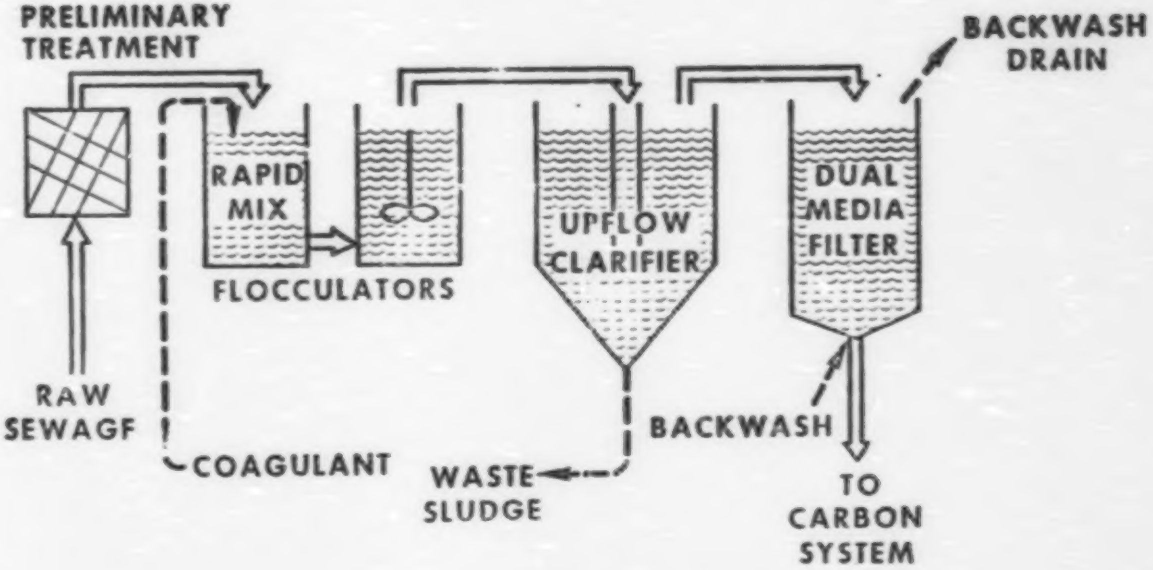

COAGULANT
RAW SEWAGE
PRELIMINARY TREATMENT
CLARIFICATION
SLUDGE TO RECOVERY SYSTEM OR DISPOSAL
FILTRATION (OPTIONAL)
CHLORINE
DISINFECTION
CARBON ADSORPTION
FILTRATION (OPTIONAL)
MAKE-UP CARBON
CARBON REGENERATION

FIG.1 FLOW DIAGRAM OF A PHYSICAL-CHEMICAL TREATMENT SYSTEM

FIG. 2

TYPICAL FLOW DIAGRAM
OF CLARIFICATION SYSTEM


PRELIMINARY
TREATMENT
RAW
SEWAGF
RAPID
MIX
FLOCCULATORS
COAGULANT
UPFLOW
CLARIFIER
WASTE
SLUDGE
DUAL
MEDIA
FILTER
BACKWASH
DRAIN
BACKWASH
TO
CARBON
SYSTEM

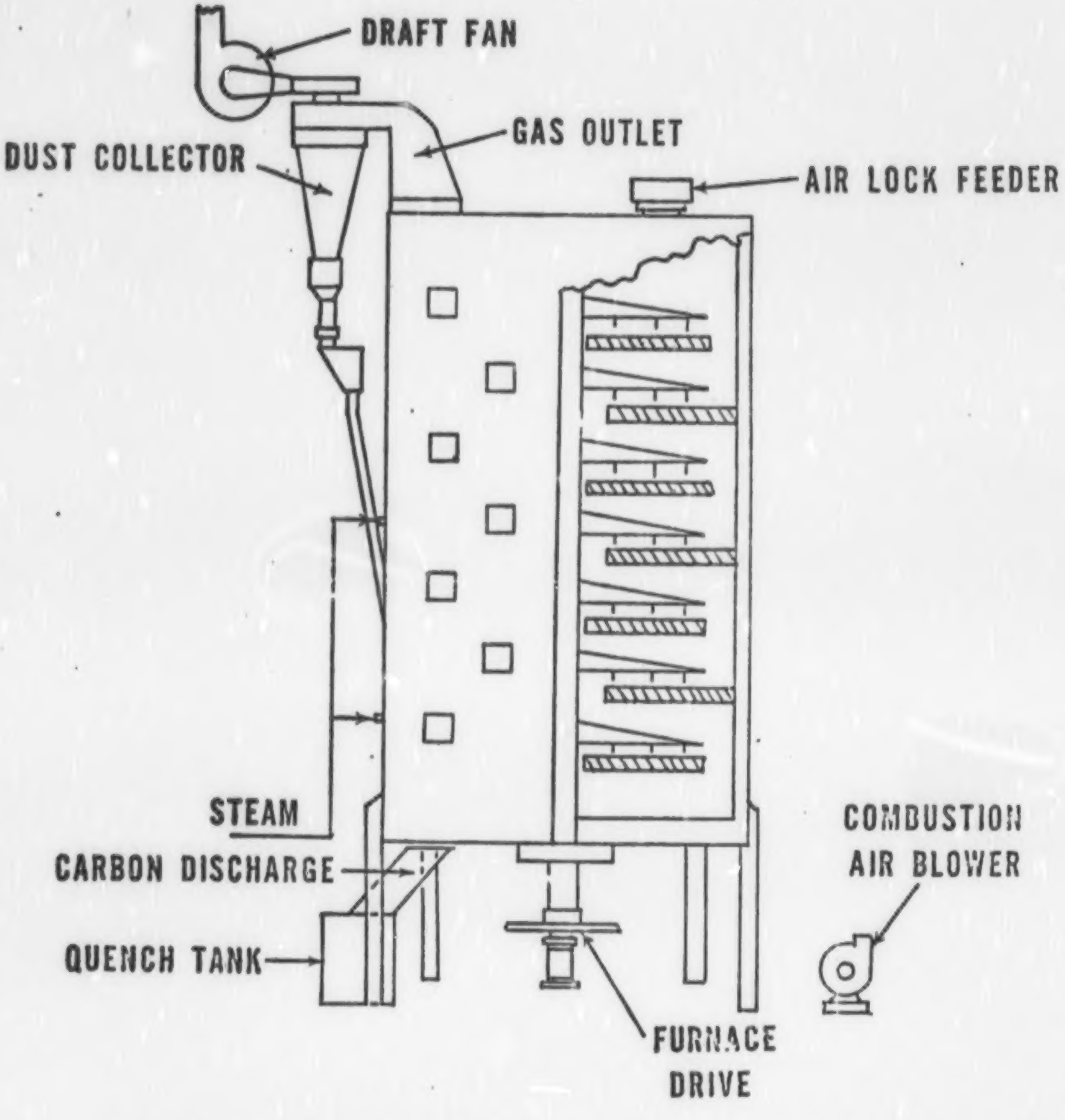

DRAFT FAN
GAS OUTLET
DUST COLLECTOR
AIR LOCK FEEDER
STEAM
CARBON DISCHARGE
QUENCH TANK
COMBUSTION AIR BLOWER
FURNACE DRIVE

FIG. 6 - MULTIPLE - HEARTH REGENERATION FURNACE

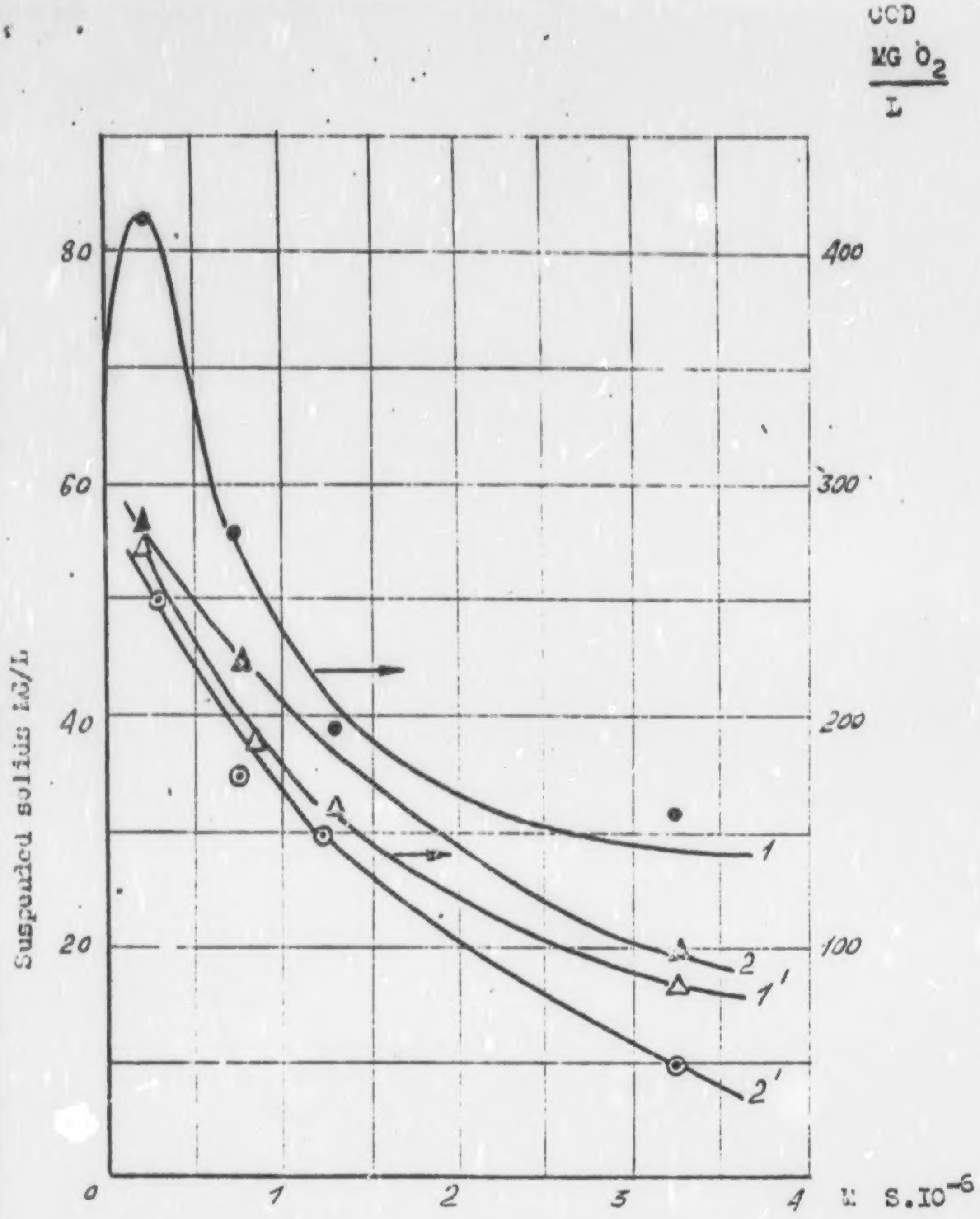


Figure I. Relationship between the sewage treatment rate and the flocculant molecular weight HPS-II

I; 2 - settling

I; 2' - flotation

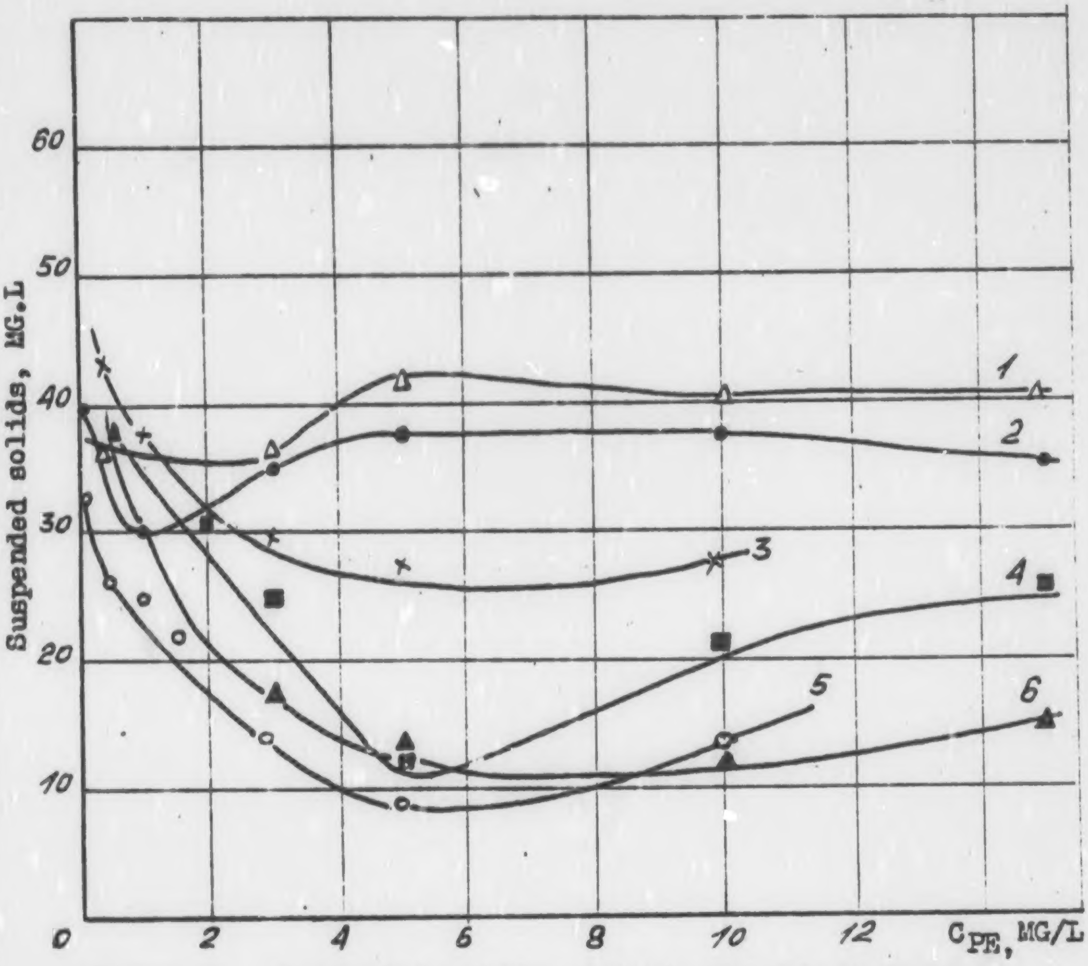


Figure 2. Suspended solids content of ballast sewage after settling depending on the flocculant dose:

I - BA - I02; 2 - BA - 2I2; 3 - PEI;

4 - BA - II2; 5 - HPS - II (Mol.weight=726000);

6 - PPS

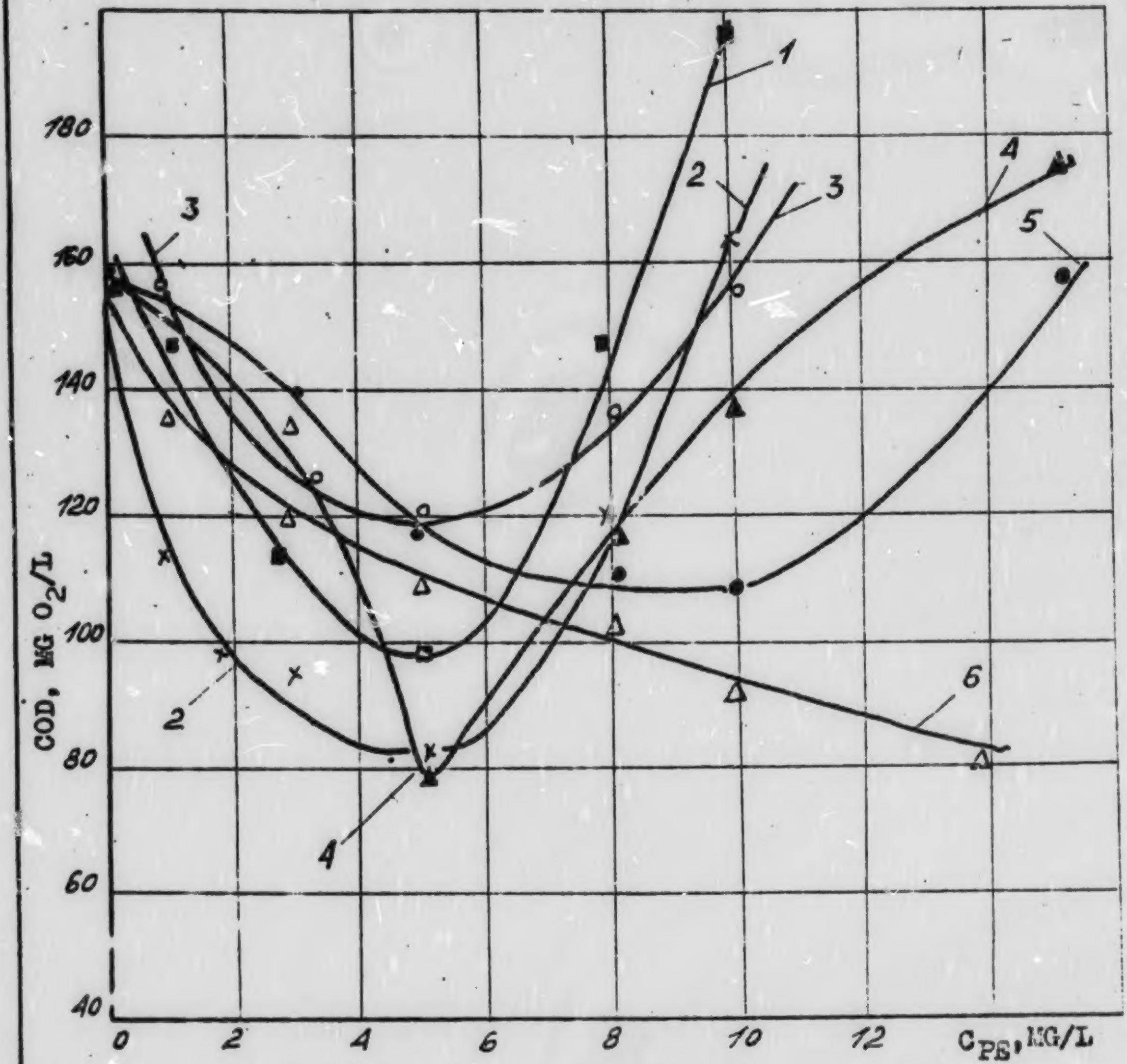
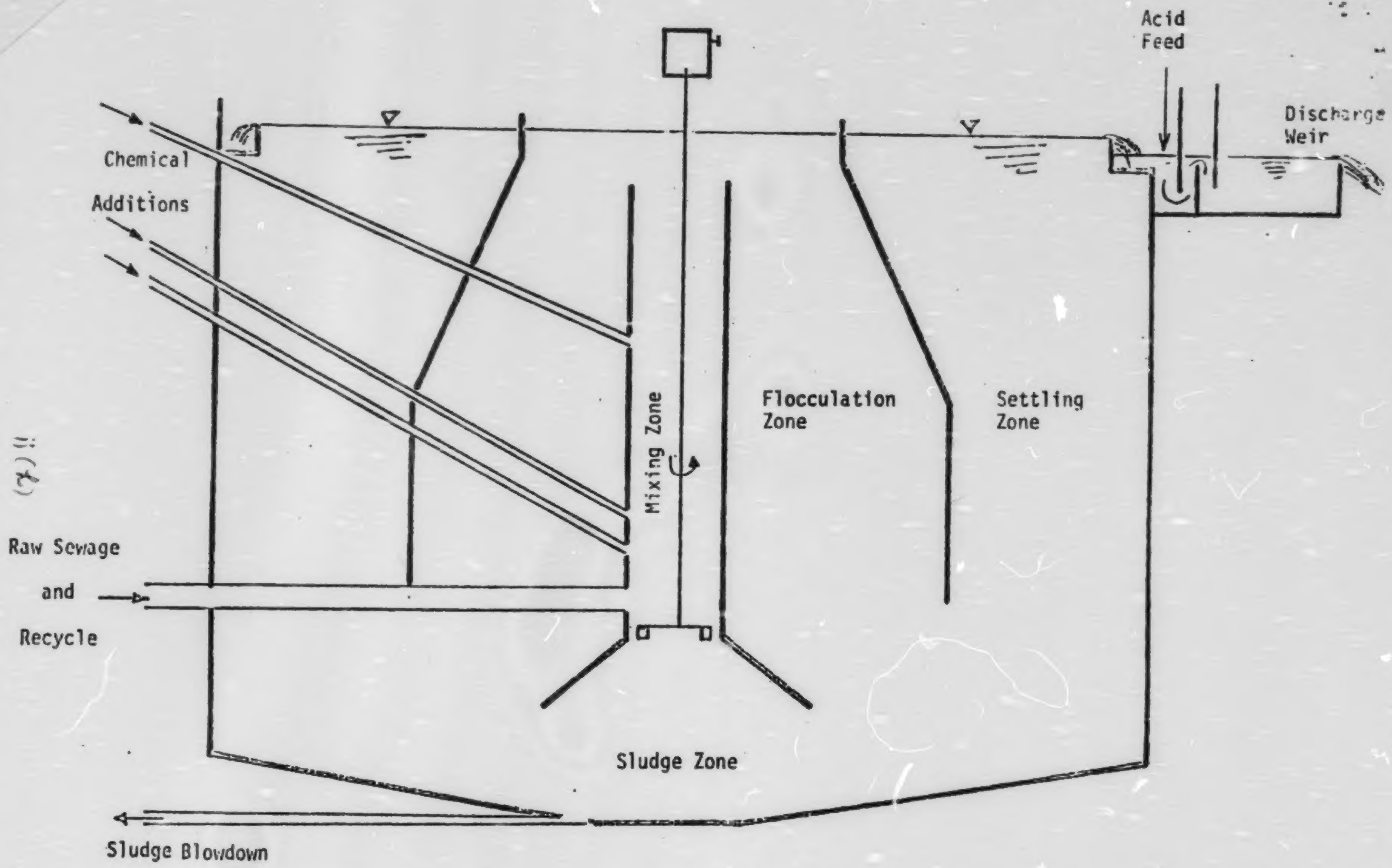


Figure 3. Relationship between the settling efficiency of the ballast COD sewage and the flocculant dose:

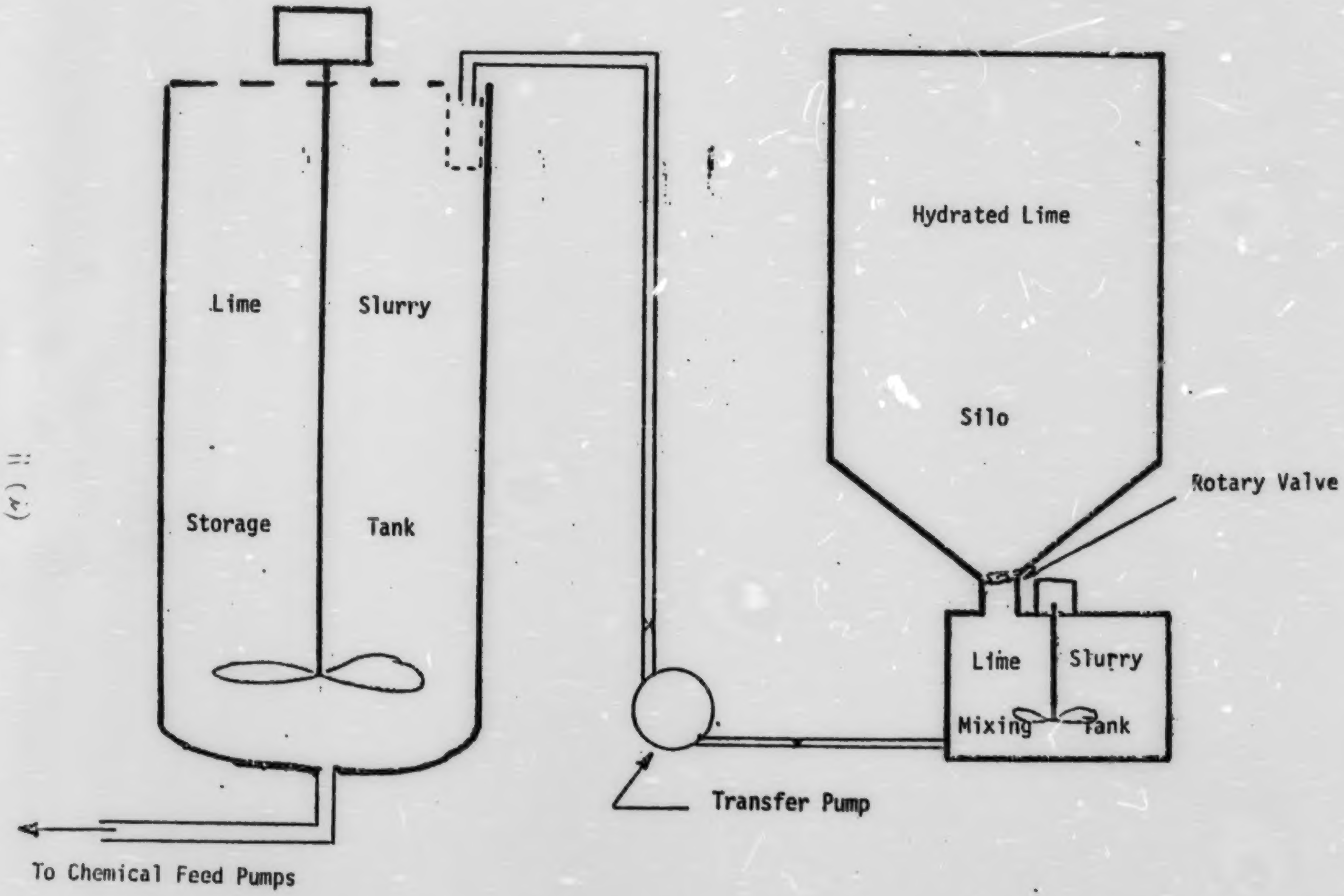
I - PPA; 2-HPS-II (Molecular weight =726.000);

3 - PEI, 4 - BA - II2; 5 - BA - I02;

6 - BA - 2I2.


Acid Feed
Discharge Weir
Chemical Additions
Mixing Zone
Flocculation Zone
Settling Zone
Raw Sewage and Recycle
Sludge Zone
Sludge Blowdown

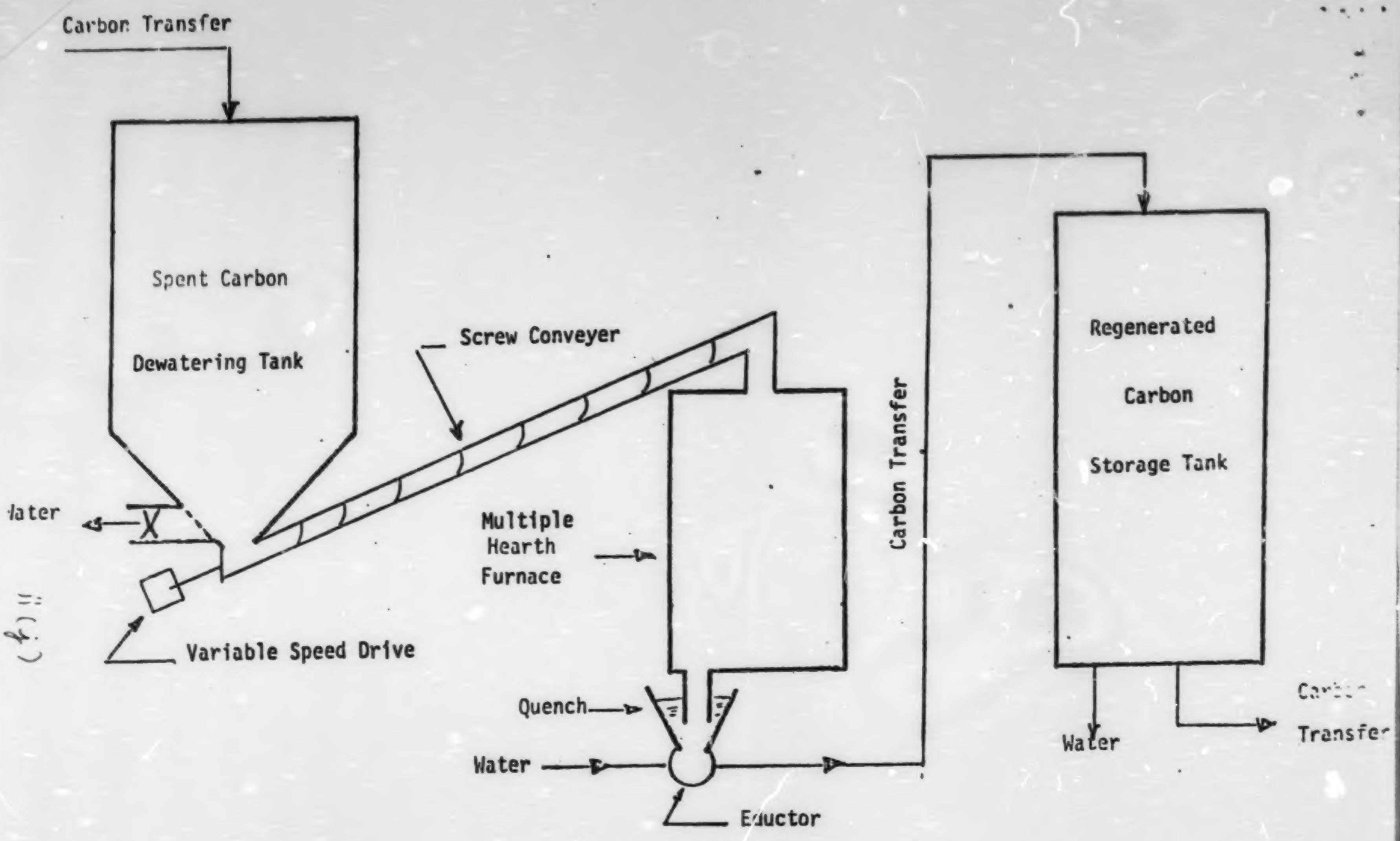
SUSPENDED SOLIDS CONTACT CLARIFIER


Lime Slurry Storage Tank
To Chemical Feed Pumps
Transfer Pump
Hydrated Lime Silo
Rotary Valve
Lime Slurry Mixing Tank

LIME SLURRY MAKEUP SYSTEM

Figure 5

Rosemount AWTP


Carbon Transfer
Spent Carbon
Dewatering Tank
Water
Screw Conveyer
Variable Speed Drive
Multiple
Hearth
Furnace
Quench
Water
Eductor
Carbon Transfer
Regenerated
Carbon
Storage Tank
Water
Transfer

ii(j)

ACTIVATED CARBON REGENERATION SYSTEM

Rosemount AWTP

Figure 6

INDEX

Press Release v

Opening Address – Dr. Andrew W. Breidenbach 1

Papers Presented at the USA/USSR SYMPOSIUM

1. Cohen, Jesse M. and Westrick, James J. (US EPA), *"Overview of Physical-Chemical Treatment"* 4

2. Maysnikov, I.N., Gandurina, L.V. and Butzeva, L.N. (Vodgeo), *"Studies on Wastewater Treatment with Flocculants Application"* 14

3. Polta, Robert (Metropolitan Waste Control Commission, Twin Cities Area), *"The Operation of the Physical-Chemical Treatment Plant at Rosemount, Minnesota"* . . . 20

4. Levchenko, M.N. (orgchim), *"Treatment of Chemical Plant Effluents"* 31

5. Weber, Walter J. Jr. (University of Minnesota), *"The Role of Activated Carbon in Physiochemical Treatment"* 35

6. Miasnikov, I.N., Balakin, B.A. (Vodgeo), *"The Removal of Volatile Suspended Solids from Wastewaters"* 50

7. Culp, George L. (Culp, Wesner and Culp), *"Design of Facilities for Physical-Chemical Treatment of Raw Wastewater"* 58

8. Korshak, V.V., Zubakova, L.B., Gandurina, L.B., Mendeleev, D.I. (Moscow Chemistry Technological Institute), *"Synthesis of Cationic Polyelectrolytes for Treatment of Natural and Waste Waters"* 76

9. Lacy, William, J. and Cywin, Allen (US EPA), *"Physical-Chemical Treatment of Wastewaters from the Petroleum Refining-Petrochemical Industry"* 81

10. Panova, V.A., Goriatchev, N.S., and Lurie, U.U. (Vodgeo) *"Examination of Oil-Containing Waste Waters Chemical Composition after their Treatment in Aeration Tanks"* 90

11. Dunlap, Robert W. and McMichael, Francis Clay (Professors, Carnegie-Mellon University), *"Comparison of Alternative Strategies for Coke Plant Wastewater Disposal"* 96

12. Belevtzev, A.N., and Maixmenko, Ju.L. (State Committee of Scientific and Technical Affairs) *"Studies on Oxidation Processes of Cyanides and Phenols in Waste and Natural Waters by Using Chlorine Dioxide"* 105

13. Gellman, Dr. Isaiah (National Council of the Paper Industry for Air and Stream Improvement), *"Current Status and Directions of Physical-Chemical Effluent Treatment in the Paper Industry"* 111

14. Ponomarev, V.G. and Zakharina, S.B. (Vodgeo), *Treatment of Concentrated Waste Waters Containing Oil Emulsions"* 120

15. Markek, Anton C. and Askins, William (American Cyanamid), *"Advanced Wastewater Treatment for an Organic Chemicals Manufacturing Complex"* 124

16. Sebastian, Frank P. (Envirotech), *"Cost Benefits of Physical-Chemical Treatment"* . . .136

Papers submitted late from May symposium in USSR

17. Ostrovsky, O.P., Souproun, U.M., Reznikov, U.N. (VNIPI Chermetenergoochistka) *"Processing and Neutralization of Industrial Wastes from Iron and Steel Effluents Treatment"* 144

18. Lukinykh, N.A. and Turovsky, I.S. (Moscow City Water Supply and Treatment), *"Fundamental Principles of Selecting the Methods for Processing Sewage Sediments in Accordance with their Properties"* 150

Protocol 154

Appendix I Participants 156

Appendix II Reports 157

Appendix III Program 158

JOINT US/USSR SYMPOSIUM
ON PHYSICAL/CHEMICAL TREATMENT
AND US TOUR
NOVEMBER 9 - NOVEMBER 23

The U. S. Environmental Protection Agency is hosting a joint US-USSR Symposium on Physical–Chemical Treatment the week of November 12-14, 1975 at the Robert Taft Research in Cincinnati, Ohio. The Symposium is being held under the auspices of the Joint US/USSR Bilaterial Environmental Agreement signed in the fall of 1972 by Presidents Nixon and Podgorny. As part of their activities in the Cincinnati area, the Soviets will be escorted through the new facilities (Environmental Research Laboratory) located at 26 Sinclair Street.

The program for the Symposium will include 9 papers on Physical/Chemical Treatment for the U.S side and 7 papers from the Soviet side.

In conjunction with the Symposium, a tour has been arranged for the 6 Soviets of several East Coast wastewater treatment facilities. The tour begins on Saturday, November 15 with visits planned for the Lamberts Point and Chesapeake-Elizabeth plants located in the Norfolk area. Monday, November 17, the Soviets will visit the Williamsburg Treatment Plant. The Soviets will visit several plants in the Harrisburg, Pennsylvania area before leaving for the Soviet Union on November 23, 1975.

Improving The Climate for Our International Environment

A SPEECH BY DR. ANDREW BREIDENBACH, ACTING ASSISTANT ADMINISTRATOR
FOR WATER AND HAZARDOUS MATERIALS,
U.S. ENVIRONMENTAL PROTECTION AGENCY,

TO THE US/USSR SYMPOSIUM
ON PHYSICAL CHEMICAL TREATMENT,
CINCINNATI, OHIO

NOVEMBER 12-14, 1975

INTRODUCTION

I am glad to be here today to speak before this distinguished bilateral group which is concerned with bringing about environmental improvement.

Both the Soviet and United States goals are similar in our large scale national efforts to clean up lakes, streams, and coastal waters, and the water that we drink. Both of our nations have had long periods of history when economic growth received such concentrated attention that the equivalent need to maintain a healthy environment was often overlooked and neglected.

I am happy to say that attention to the environment has taken a healthy turn for the better in each of our countries. The work of this group is dramatic evidence of this fact, and I wish you all success in your efforts. Already, the interchange of information and visits between the USSR and US participants have led to worthwhile results. Each country has its own area of outstanding expertise in environmental improvement that we can share to our mutual benefit. Each country has developed leads in technologies for water pollution abatement that would have taken a long time and significant expense to match if the information were not to be inter-communicated.

Jointly, we have been determining where each of our nations stand in controlling the major industries manufacturing iron and steel, pulp and paper, chemicals and petroleum refining where the major part of our industrial pollution occurs. And we can begin identifying the specific areas of pollution abatement technology that would provide the most benefit to our respective nations, so we can concentrate our attention efficiently.

In municipal wastewater treatment control, we have passed this stage and have begun to exchange information on control methodologies that are most beneficial. Municipal treatment, of course, is where our citizens become even more directly involved in our efforts and where the costs are directly borne through local, state and federal bonding and tax revenues.

While on this subject, I am happy to note that citizen support for our environmental improvement measures has continued at a high level.

SUPPORT OF ENVIRONMENTAL IMPROVEMENT

Certainly, it is true that progress in improving the environment cannot be sustained without the heartfelt support of the citizens in each of our countries. I am greatly encouraged by the fact that the United States' program has been characterized by consistent, sustained public support for environmental goals and efforts to achieve those goals.

As you may know, one of the methods we use to determine the desires and opinions of our citizens is the polling of public opinion where we go out to segments of the public and sample and record the response. On the issue of the impact and cost of environmental controls, all along, public opinion polls have demonstrated considerable support for our environmental programs—even during the recent period of recession and rising prices. I am most heartened by the fact that this support has not been fickle. In fact, a survey by a major opinion research firm in August showed that 60% of the public believe it is more important to pay the costs to clean up the environment than it is to keep prices and taxes down. And 90% say that if the environment is not cleaned up now, it will cost more in the long run.

To me this is a dramatic public endorsement of our efforts. I am happy to say that President Ford has given high priority to the environmental effort and has repeatedly supported requests for increased manpower and funding. The Congress has also consistently acted to indicate its support. And the States and local governments have joined in the national efforts with their own funds and programs.

GOALS

The specific goals of the United States program are swimmable and fishable waters by 1983 and no discharge of pollutants by 1985. The U.S. Congress has had the National Commission on Water Quality working on the feasibility of these goals over the last two years and we will shortly be receiving the final report of the Commission. Presently, the draft report of the Commission's staff answers the question as to whether or not achieving the goals of our Federal Water Pollution Control Act of 1972 will be too expensive for the economy of the United States.

The staff report found that the "impacts of the projected expenditures on water pollution abatement on the general economy–GNP growth rate, general price level, interest rates, etc.–are not significant."

In an analysis of the price impact of PL 92-500, the report found that the annual price increase, at an average, would be 3/10 of one percent–a very small price, indeed, to pay for cleaner water.

And it must be remembered that the municipal wastewater treatment construction grant program, amounting to $18 billion, is creating more jobs, with some 125,000 on-site and off-site jobs having already been created as a result of the construction grant program. That figure is expected to rise to 200,000 by the end of fiscal year 1977. The multiplier effect in other sectors of the economy will considerably augment that figure.

EVIDENCE OF IMPROVEMENT

It is well to recognize that the kind of tangible results we hope and expect to see resulting from PL 92-500 will not show up overnight. We are, in a sense, in mid-stream in this effort. The enormity of the task was not anticipated either by the Congress or by the agency, and we will require the dedication of more resources in funds and people to the achievement of the goals.

Meanwhile, we can take heart at the successes we are beginning to record in this effort, all across the nation. We are moving, and we are moving in the right direction.

Just a decade ago, Lake Erie in our great lakes had been given up for "dead" by biologists. And the Escambia Bay in Florida faced a similar prognosis. In both cases, federal, state and local efforts have dramatically revived both bodies of water to the point where fish life–and some species not seen for many years–not only survives but is thriving.

In these and many other areas individuals are enjoying once again the pleasures of cleaner water and the success of the water clean-up effort is being recorded.

Over 97% of all water discharges are either now in compliance with pollution control standards or are on definite water clean-up schedules–with these requirements backed up by strong penalties for violations. Among this number are almost all of our big industries.

Over 4,000 individual municipal wastewater treatment projects are now underway–and improvements in the administration of the construction grants program will move these and other new projects to successful completion.

We are, in effect, winning the first round in the fight to end water pollution.

FUTURE EFFORTS

The next round will be much more difficult and more costly–because it will deal with pollution from sources that will require not only the application of enormous resources, but also the application of technologies that are still being developed and are not often available.

In our construction grants program for building treatment facilities for urban wastewaters, it is estimated that only 50%, or some 9,000 of 18,000 municipal treatment plants, will provide by 1977/78 the necessary quality of treatment. Moreover, these 9,000 plants represent less than 40% of the 1977 population because the larger cities will not have completed necessary construction by that time. Our figures indicate that it will take over $46 billion to raise treatment up to secondary, or higher, where required by water quality standards.

In the case of industry it is tentatively estimated by the National Water Quality Commission that it will take somewhere between $59.6 billion and $174.8 billion to eliminate pollution from industry sources. These are preliminary figures, however, and they appear to be on the high side.

Also, while on this subject, we are particularly concerned about the problem of eliminating toxic and hazardous industrial effluents from wastewaters that are discharged directly into our waters or which go into municipal treatment systems which are not prepared to treat these special discharges. It will require a complex and innovative effort to develop the necessary technologies to treat industrial wastes in many cases.

As part of our control effort for instance, our guidelines for pretreatment standards, which are being developed, will be presenting information on those chemicals that would inhibit the treatment plant processes. This approach would allow the individual plant manager to set the criteria for influents into his plant to prohibit any chemical, or level of chemicals, that would damage his plant operations.

The development of more and more new industrial chemicals makes this task of protecting our environment and public health more and more difficult. Fortunately, this group gathered here today will help to make the task more easily and quickly accomplished. The problem of industrial wastes and the special needs of treatment are common to both of our countries. The progress that we make exchanging ideas and innovations will reinforce pollution abatement progress not only for our nations–but for all nations on our earth. I see by the agenda that the variety of important subjects and topics to be discussed should significantly contribute to further progress and achievements, and I am pleased to express the appreciation of the United States for the participation of our Soviet colleagues.

THE CINCINNATI CENTER

One final thought before concluding, EPA is heavily committed to research efforts in the field of water pollution abatement. And health effects research is one area that will be receiving increased emphasis. I am happy to have been a party to these activities and to have worked to build the new laboratory center, here in Cincinnati, which you have toured. Although not quite finished, it was dedicated by President Ford and Mr. Train, our EPA Administrator, during the past summer.

Already, research conducted in Cincinnati has shown us how to prevent the growth of algae by removing wastewater nutrients; clean up oil spills; and produce safe drinking water, among other discoveries. And we have extended the improvements through EPA's technical assistance programs, to communities and states all across America.

We hope these and the future improvements we expect to develop in wastwater treatment will be similarly beneficial to the Soviet citizens. I assure you we will effectively employ advances in research due to the Soviet efforts, and while we continue these exchanges, I am mindful we are not only eliminating wasteful duplication of effort but communicating the benefits of our different approaches to improving abatement controls and furthering the cause of cooperation for environmental improvement throughout the world.

Thank you.

Overview of Physical–Chemical Treatment

Jesse M. Cohen*
James J. Westrick

INTRODUCTION

A little more than a decade of research has resulted in significant changes in the technology of treating municipal wastewater. The design engineer now has process alternatives not available to him in the past. These processes, based largely on physical–chemical principles, have the capability of treating a wide variety of wastewaters to produce effluents ranging in quality from "secondary" as defined by EPA to that which would meet the most stringent state requirements. These processes, in conjunction with biological processes, are increasingly being used to produce effluents that are suitable for reuse, including use as a source for potable water.

The treatment system which is most advanced in development is the series of unit processes illustrated in Fig. 1 (1,2). Following conventional pretreatment such as bar screening and grit removal, the raw sewage is treated with a metal coagulant or precipitant which effectively removes suspended and colloidal solids as well as phosphates. This unit process also removes most, but not all, metals. Filtration through granular media, optionally located either before or after carbon adsorption, further reduces suspended solids. In some plant designs the filtration step is omitted, and the downflow carbon contactors serve the dual purposes of filtration and adsorption.

The fully clarified effluent from chemical treatment is contacted with activated carbon which removes dissolved organic matter. Where required, disinfection, usually with chlorine, completes the treatment system. When the carbon has been exhausted and can no longer produce the desired effluent quality, it is removed from the contactor and thermally regenerated. Sludges produced during chemical clarification are processed for disposal.

CHEMICAL CLARIFICATION

Clarification Equipment

Chemical clarification is the initial series of operations in a physical-chemical system. The processes are essentially the same as those traditionally used in water treatment practice. A common flow scheme for clarification is shown in Fig. 2. Chemicals and wastewater are mixed in a rapid mix basin which provides about one minute detention at average flow. Mechanical mixing is preferred to ensure complete dispersion of the chemical in the wastewater. From the rapid mix basin the coagulated wastewater then flows to a gently stirred basin where it is retained for 10-15 min to allow the particles to collide, adhere and grow to a settleable size. Slow paddle mixers are commonly used for this application. The flocculated water is then directed to a clarifier where quiescent conditions permit the solids to settle out. In many cases, it is advantageous to recycle settled sludge to the rapid mix basin in order to assist in precipitation and floc formation. The remaining sludge is withdrawn for dewatering and disposal.

Chemicals for Clarification

Several chemicals may be used alone or in combination for wastewater clarification. These are listed in Table 1 and include lime at various pH's (3,4), salts of iron and aluminum (5), and organic polymers. The choice of the chemical to use depends on several factors listed in Table 2. All factors are ultimately based on optimizing process economics to reach a desired water quality (6).

The chemistry of coagulation-flocculation has been extensively described in the literature (7). Typical results of these reactions can be illustrated by a description of ferric chloride treatment of raw wastewater shown in Fig. 3 (5). Increasing dosage of ferric chloride, expressed in the illustration as Fe^{3+}, results in precipitation of phosphorus as ferric phosphate. Here, the optimum dose for phosphorus precipitation was about 60 mg/l of Fe^{3+}. Concurrently, ferric hydroxide is formed which coagulates and flocculates the suspended and colloidal solids. Minimum residual turbidity obtained here coincided with the optimum for phosphorus removal at a dose of 60 mg/l. Since the chemical hydrolysis of ferric chloride consumes an equivalent amount of alkalinity, pH of the effluent will decrease, depending on the buffering capacity of the wastewater. In this instance, pH decreased from about 7.8 to 6.5 at optimum iron dosage. In addition to suspended and colloidal solids flocculation, chemical treatment also removes 20-35 percent of dissolved organic matter expressed here as soluble COD.

Since each wastewater is unique in its chemistry, the exact dosage of chemical required must be determined for each wastewater. This determination can readily be made by appropriate jar tests of all chemical options. After the dosage has been determined, then other factors such as cost of chemical and sludge disposal, can be considered for the final choice of chemical.

Use of iron or aluminum salts results in a change in composition of total dissolved solids. Depending on dosage, some 50-100 mg/l of additional chloride or sulfate ion occurs in the effluent, while 20-30 mg/l phosphate ion and 50-100 mg/l of carbon dioxide are removed, thus resulting in little or no net increase in total dissolved solids. Lime, on the other hand, can result in lowered total dissolved solids through softening reactions that reduce calcium and magnesium content.

FIG. 3
$FeCl_3$ TREATMENT OF RAW WASTEWATER

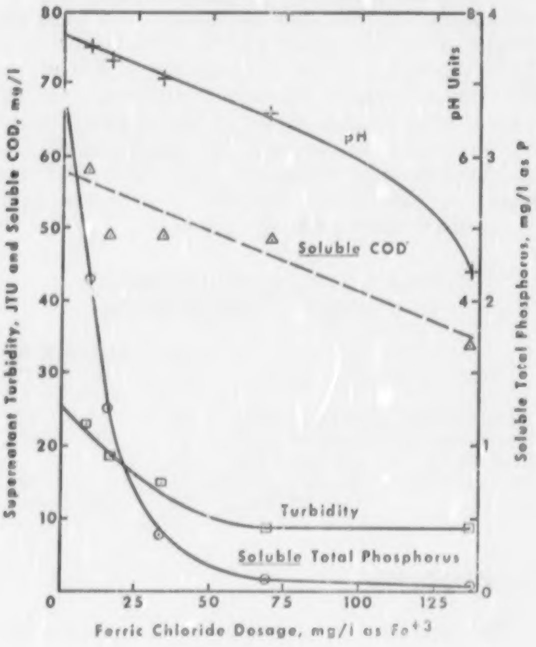


TABLE 1. CHOICE OF CHEMICALS FOR CLARIFICATION

1. Ferric Chloride
2. Ferrous Sulfate Plus Base
3. Ferric Sulfate
4. Aluminum Sulfate (Alum)
5. Lime (Single-Stage)
6. Lime (Two-Stage)
7. Waste Pickle Liquor Plus Base
8. Sodium Aluminate
9. Organic Polymers

Note: Polymers frequently added to assist flocculation

TABLE 2. FACTORS AFFECTING CHOICE OF CHEMICALS

1. Influent Phosphorus Level
2. Effluent Discharge Standard
3. Wastewater Characteristics
4. Plant Size
5. Chemical Costs Including Transportation
6. Sludge Handling Facilities
7. Sludge Disposal Facilities
8. Other Processes Utilized

Performance of Clarification

Chemical clarification, properly conducted, transforms raw wastewater to a fully clarified effluent with substantially reduced concentrations of phosphorus, organic matter and metals. Typical results are shown in Table 3 which provides data obtained at five plants. Clarification typically removes 70-80 percent of the organic matter, 90-98 percent of suspended solids and 80-98 percent of the phosphate (8). Lesser removals may be obtained when chemical dosages are reduced and when the wastewater contains a higher-than-usual proportion of dissolved organic matter.

TABLE 3. TYPICAL PERFORMANCE OF CHEMICAL CLARIFICATION

Plant	Chemical	Organic Rem. %	SS Rem. %	P. Rem. %
Ewing-Lawrence	170 mg/l $FeCl_3$	80	95	90
New Rochelle (ZM)	Lime pH 11.5	80	98	98
Westgate, Va.	125 mg/l $FeCl_3$	70	–	–
Salt Lake City	80-100 mg/l $FeCl_3$	75	–	80
Blue Plains	Lime pH 11.5	80	90	95

Sludge Production

The addition of chemicals to raw wastewater obviously increases the weight of sludge produced, compared to simple gravity sedimentation, because of greater removals of suspended solids and because of the presence of precipitated hydroxides, carbonates and phosphates. The total weight of sludge produced can be estimated in several ways: by weighing the sludge from a jar test or pilot facility or by calculating the amount from a knowledge of the precipitation products and suspended and colloidal solids removed. As a rough approximation, the weights of chemical sludge produced per unit weight of coagulant fed are: 0.86 for ferric chloride, 0.36 for alum and 1-1.5 for hydrated lime (9).

Both the volume and weight of sludge produced by chemical treatment of raw wastewater can vary substantially from plant to plant because of varying wastewater characteristics, kind and dosage of chemical used and the type and method of operation of clarification equipment. Data from several pilot plant and full-scale operations are summarized in Table 4.

In order to put chemical sludges in the context of familiar experience, the combined sludges produced by conventional primary and secondary biological treatment are included in the summary. In terms of sludge volume, chemical and biological sludges are comparable. Low pH lime precipitation will, in fact, produce less than half the volume than combined biological sludge. In terms of weight of dry solids, lime processes produce 2-4 times as much of sludge as biological, while iron and aluminum precipitation will produce as much or one-half as much. Another characteristic shown in Table 4 is sludge solids concentration. Lime sludges are characteristically high in solids ranging from 4.4-11.1 percent. Sludges produced by iron or aluminum salts range for 1.2-2.25 percent which are comparable to the mixed primary and waste activated sludge (10).

Chemical sludges, like primary and waste activated sludges, can be handled in the usual ways; thickened, digested (except for high pH lime), dewatered, landfilled, land spread or incinerated. All of these approaches are being considered in design of full-scale plants or are in operation. A more complete description

TABLE 4. SLUDGE CHARACTERISTICS CHEMICAL TREATMENT OF RAW SEWAGE

	Sludge Solids %	Wt. of Solids lb/MG	KG/m^3	Volume of Sludge 1b/MG	1/m^3
Primary & Waste Activated Sludge	1.0	2,200	0.26	22,000	22.0
Lime, low pH	11.1	5,630	0.680	8,924	8.9
Lime, High pH	4.4	9,567	1.15	28,254	28.2
Aluminum	1.2	1,323	0.159	23,000	23.0
Iron	2.25	2,755	0.333	21,922	21.9

Average of data from Blue Plains, Lebanon, Taft Center, Salt Lake City.

of sludge production and disposal is contained in an EPA Technology Transfer publication entitled "Process Design Manual for Sludge Treatment and Disposal." (11).

GRANULAR MEDIA FILTRATION

The effluent from a chemical clarifier operating on raw sewage will normally contain a small amount of suspended solids, on the order of 25 mg/l or less. These suspended solids can be removed by filtering the clarifier effluent through a bed of granular media (12). In some system designs, that granular bed is a carbon contactor, acting as both an adsorber of dissolved organics and as a filter of suspended solids. Carbon contactors, however, are often quite deep, e.g. 12-16 ft (4-5 m), and cleansing the bed of accumulated solids can be difficult. Also, there is no way to protect the carbon against upsets in the clarifier which could lead to rapid plugging of the bed. Finally, a packed bed of carbon is an inefficient filter because the particle size gradation will be hydraulically classified from finer particles at the top of the bed to coarser particles at the bottom. Thus, many designers prefer to assign the filtration role to a granular media filter specifically designed for that single purpose.

A granular media filter could also be placed after an adsorption system (13). For example, upflow expanded bed granular carbon systems do not remove solids. Moreover, such systems may in fact produce a small amount of additional solids in the form of sloughing biomass. Therefore, positioning the filter after fluidized or expanded bed carbon contacting would provide for removal of clarifier effluent solids (which pass through the fluidized bed) and also any turbidity resulting from the development of sloughing of biomass on the carbon. Granular media filters are almost essential as a final treatment step in powdered carbon systems in order to prevent substantial quantities of the very small carbon particles from being discharged in the effluent (5).

GRANULAR ACTIVATED CARBON

The principal role of activated carbon is the removal of soluble organic material from wastewater. This is accomplished primarily by the physical adsorption of organic molecules on the surfaces of the carbon, which is a material uniquely suitable for this purpose. The high capacity for adsorption by carbon is derived from its very large internal surface area (600-100 m^2/g) and its special surface properties which form during the activation process. When the capacity of the carbon surface to remove additional molecules is diminished to a predetermined extent, the surface can be renewed by treatment of the carbon in a thermal regeneration system, where the adsorbed organic molecules are volatilized or oxidized and driven off the carbon. The carbon, thus reactivated, is reintroduced into the adsorption system and reused. A typical flow diagram illustrating the series of operations is shown in Fig. 4.

Maximizing Carbon Utilization

There are two fundamental objectives of carbon contactor design. The first is to maintain wastewater and carbon in contact for a sufficient period of time to achieve the desired degree of organic removal. Most studies on municipal wastewater have indicated optimum contact times in the range of 20-40 min (based on empty bed volume). The second objective is to provide that contact in such a way as to maximize the utilization of the capacity of the carbon to remove organics and thus minimize the replacement rate (14).

From an adsorption standpoint, maximum utilization of the carbon capacity is obtained by the use of countercurrent operation. An examination of the Freundlich equation, an empirical relationship that has been shown to adequately describe equilibrium data, will show why:

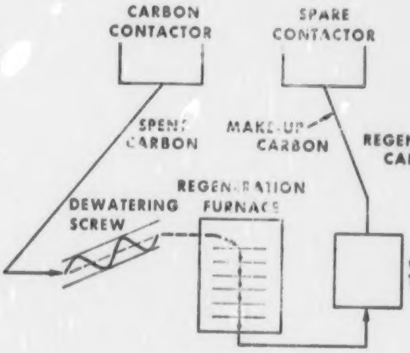
$$\frac{X}{M} = kC^{1/n}$$

where X = weight of organics adsorbed
M = weight of carbon applied
C = concentration of organics in solution at equilibrium
k,n = empirical constants

This equation shows that the carbon loading, $\frac{X}{M}$ (amount adsorbed per unit weight of carbon), increases as the equilibrium concentration of the organic material in the solution increases. In countercurrent contacting the carbon and the wastewater move through the contactor in opposite directions. Thus, carbon just leaving the contactor is in equilibrium with

FIG. 4

ACTIVATED CARBON REGENERATION SYSTEM



wastewater with the highest carbon loading, $\frac{X}{M}$, possible. Fresh carbon just entering the system contacts the wastewater lowest in organics and provides the best possible effluent at that contact time.

Since it is difficult in practice to achieve continuous countercurrent contacting, adsorption system designs approximate countercurrent contacting by using pulsed bed, multiple-staged series operation, or single-stage parallel contacting.

Pulsed-bed operation is a close approximation to continuous countercurrent contacting. Here wastewater flows up through a packed carbon bed. Slugs of spent carbon are periodically removed from the bottom of the adsorber and replaced at the top with fresh carbon. The system is analogous to incorporating a large number of stages within a single contactor. This type of carbon contacting is commonly used as a "polishing" step to handle highly pretreated wastewater essentially free of suspended solids.

The two most commonly used designs for treating chemically clarified raw wastewater are shown in Fig. 5, which illustrates single and two-stage contacting. As the number of stages increase, the more closely countercurrent contacting is approached. However, more than two stages generally become uneconomic because of the complex piping and valving.

Series contacting essentially divides an adsorber into a number of contactors in series. When the effluent standard is reached or exceeded, the carbon in the lead contactor is removed and replaced with fresh (virgin or regenerated) carbon. That contactor is then positioned as the trail column and all other contactors are advanced one position in the train.

Single-stage contacting divides the total contactor volume requirement into a number of parallel contactors. By starting the contactors in staggered sequence, it is possible to have on stream at any given time contactors in various stages of exhaustion. Thus, poorer quality effluents from more heavily loaded contactors can be blended with higher quality effluents to produce the desired effluent quality. When the blended effluent quality reaches the allowable limit, the carbon in the contactor which has been on stream the longest is removed and replaced with fresh carbon (15).

Biological Activity

A major factor in the operation of granular carbon systems on chemically clarified raw wastewater is the potential for the development of biological growths in the carbon. These growths can cause severe plugging problems in very short times. Therefore, packed-bed contactors should be designed so that they can be very thoroughly backwashed. Auxiliary backwash aids such as air-scour and surface wash should also be installed.

The biological growths in the carbon columns, which cause plugging and headloss problems, also can extend the life of the carbon. Carbon granules tend to serve as an attachment medium for the microbes while also providing an enriched concentration of substrate by adsorption. The mechanism of the adsorption-biological activity interaction is not clear, but carbon loadings far in excess of those predicted by laboratory isotherm tests have been observed in pilot tests conducted over a long enough time for the biological activity to develop (16).

An adverse effect resulting from biological activity is the production of the highly undesirable compound, hydrogen sulfide. Several methods have been suggested to cope with this problem and all have exhibited varying degrees of success. The one procedure which has been successful is addition of oxygen in the form of nitrate, which can be added as sodium nitrate. At the Pomona, California pilot facility, 33 mg $NaNO_3$/1 (19 mg/1 as oxygen) plus daily backwashing of the column to reduce solids accumulation, completely prevented the formation of sulfide (17). Concurrently, nitrate was reduced to nitrogen gas. An unexpected, but welcome, result of nitrate addition was the extension of the life (capacity) of the carbon. The carbon column was operated for 18 months without replacement and without a significant decline in organic removal efficiency. The apparent loading during that time reached a phenomenal 3.5 g COD removed/g carbon of which 1.54 g/g was soluble COD. Considering that values in the range of 0.5 g COD removed/g carbon are commonly accepted for carbon loading in physical-chemical systems, it is apparent that the mechanisms of filtration (2 g COD/g carbon due to particulate COD) and nitrate assisted biological activity contributed greatly to the organics removal.

Carbon Regeneration

When activated carbon can no longer produce the required effluent quality, it must be removed from the adsorption system, transported to a regeneration system and restored to nearly its original condition. In municipal wastewater treatment, regeneration of granular carbon is accomplished thermally in a multiple-hearth type of furnace (18). A typical furnace is shown in Fig. 6. The regeneration system consists of dewatering equipment, a feed conveyor, the furnace, a steam generator, a product quench tank and air pollution control equipment. Spent carbon enters the top hearth and is dried. As the carbon progresses down the hearths and its temperature increases, adsorbed organics are volatilized or pyrolyzed, leaving a char residue. Steam is injected into the furnace to oxidize the char residue and to restore the surfaces of the carbon to nearly its original condition.

During regeneration some loss of carbon is experienced through physical attrition and burning of carbon. These losses can amount to 3-8 percent or more of the volume of carbon and are an important part of the economics of carbon technology, since fresh carbon must be added to maintain adsorption capacity.

Additionally, changes in the physical characteristics of carbon are incurred during successive loading and regeneration cycles (19). These changes are illustrated in Table 5. Mineral components of adsorbed organics and particulate inorganic material contribute to the increase in ash of the regenerated carbon. Progressive changes also occur in the basic pore structure of the carbon particle. Surface contributed by small pores - >10 Å - < 28 Å as measured by Iodine Number - tends to decrease while surface contributed by the larger pores - > 28 Å as measured by Molasses Number, tends to increase. Little or no changes occur in the bulk density. In spite of these measured changes, the net effect on the capacity of carbon to remove organics is relatively unaffected.

TABLE 5. CHANGES IN CARBON PROPERTIES ON SUCCESSIVE REGENERATIONS

Cycle	Ash Content, %	I_2 No.	Molasses No.	Bulk Density, g/cc
Initial	5.7	1090	250	0.469
1	7.6	1040	310	0.468
2	8.6	935	290	0.469
3	9.5	940	350	0.473

Thermal regeneration of carbon produces a gaseous effluent containing carbon particles and noxious gases. Both must be controlled to avoid pollution of the atmosphere. Air pollution was successfully controlled at the Pomona, California pilot plant system by the system shown in Fig. 7 (17). Flue gases from the furnace first periodically discharges the accumulated dust by automatic reversal of the air flow. The particle free gases pass through an afterburner operated at 1300-1400°F (700-760°C) which incinerates the organic material which was volatilized from the carbon. Other systems have used a water spray system to remove particulates but also include the afterburner.

POWDERED ACTIVATED CARBON

Activated carbon is also produced in powdered form (passing 300 mesh, 85 um). Recent research studies have established that powdered carbon can be used successfully to treat wastewater (20,21,22). Application of this technology has lagged behind that of granular carbon primarily because regeneration of powdered carbon has only recently been demonstrated. With this development, application of powdered carbon technology need not be deterred.

Contacting Systems

Because of its small particle size, powdered activated carbon (PAC) must be contacted with wastewater as a slurry. Rate of adsorption onto PAC is very fast, equilibrium being reached in less than 10 minutes. Generally, the same kind of equipment used in chemical clarification can be used for carbon contacting. A common type of equipment is a solids-contact clarifier which can be used to mix, flocculate and settle the powdered carbon. In addition, this kind of equipment allows the development of a carbon sludge with a residence time in the contactor of several days, thus promoting the development of biological activity which, as was discussed earlier, contributes greatly to carbon's capacity to remove organics (5).

After gravity clarification, the wastewater should be directed to a granular media filter for final polishing and, more importantly, for capture of powdered carbon particles that escape the clarifier, and would otherwise be lost from the system.

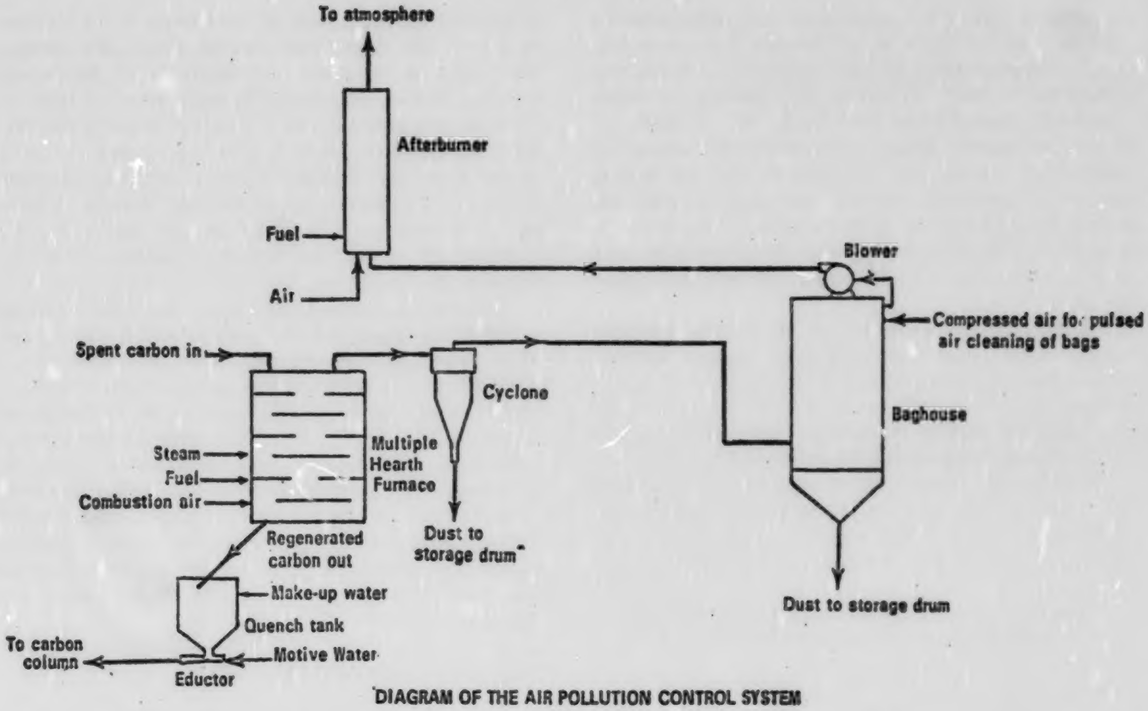
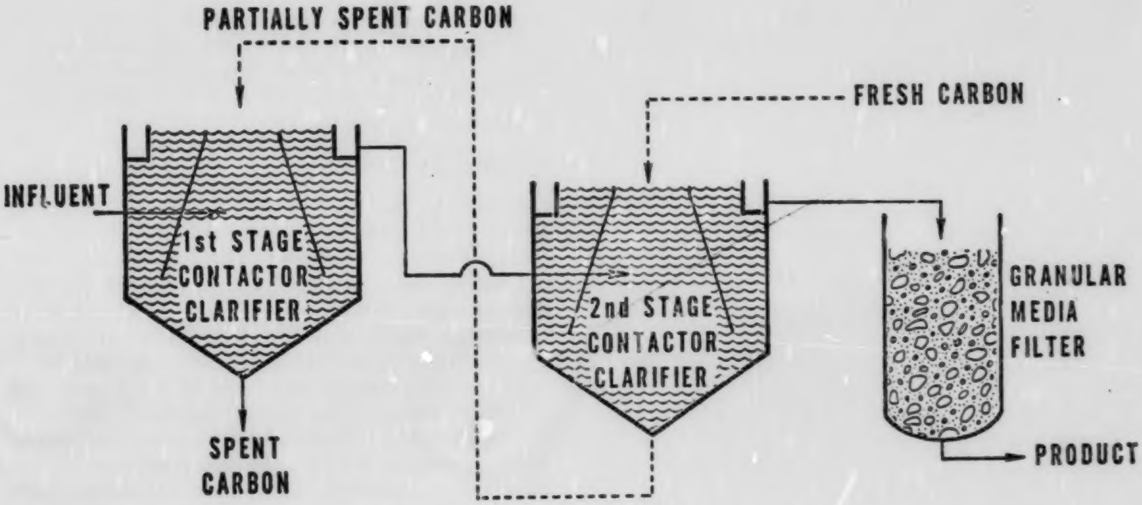

To atmosphere
Afterburner
Fuel
Air
Blower
Compressed air for pulsed air cleaning of bags
Spent carbon in
Cyclone
Baghouse
Steam
Fuel
Combustion air
Multiple Hearth Furnace
Regenerated carbon out
Dust to storage drum
Make-up water
Quench tank
Motive Water
To carbon column
Eductor
Dust to storage drum

DIAGRAM OF THE AIR POLLUTION CONTROL SYSTEM
FIG. 7


PARTIALLY SPENT CARBON
FRESH CARBON
INFLUENT
1st STAGE CONTACTOR CLARIFIER
2nd STAGE CONTACTOR CLARIFIER
GRANULAR MEDIA FILTER
SPENT CARBON
PRODUCT

FLOW DIAGRAM
TWO-STAGE COUNTERCURRENT
POWDERED ACTIVATED CARBON SYSTEM
FIG. 8

Carbon Utilization

Adsorption - and concurrent biological activity - normally takes place in a completely mixed vessel, which can consist of a single stage of contact. To obtain higher carbon loadings, two-stage countercurrent contacting is desirable for high product quality. The rationale here is the same as described for granular carbon. A typical two-stage countercurrent contacting system is shown in Fig. 8. This system can treat raw wastewater directly or be preceded by a chemical clarification system much as is used for the granular carbon system. Fresh carbon is added at the downstream clarifier, and is removed from the system as a sludge from the first contactor. Carbon solids separation may be obtained by metal coagulants or preferably by organic polymers, since the latter contributes no ash when the carbon is regenerated. In some instances, flocculation occurs unaided and is adequate if the clarifiers are operated at low overflow rates.

Regeneration

Within the past 2-3 years, it has been shown that powdered carbon can be successfully regenerated (22,23,24). The carbon sludge removed from the solids-contact clarifier, is generally gravity thickened and then dewatered. A vacuum filter has successfully produced a carbon cake of about 23-25 percent solids. Regeneration has been demonstrated in several types of thermal devices, including fluidized bed reactor containing an inert medium, transport reactor (commercial installation regenerating 10 tons/day [9000 kg/day]), in a multiple hearth furnace and in a wet-air oxidation system.

APPLICATION OF PHYSICAL-CHEMICAL SYSTEMS

Extensive bench and pilot scale research during the past decade has resulted in physical-chemical systems which are technically and economically feasible alternatives to biological systems. At the present time some fifteen full-scale plants are in various stages of design and construction, all of which will treat domestic/industrial wastewater. Three plants are in the initial stages of operation. Additionally, at least 12-15 plants are being designed or constructed which will apply physical-chemical systems to biological effluents to produce very high quality effluents (15).

The reasons for choosing physical-chemical systems over the alternative biological treatment are generally based on the several advantages that physical-chemical systems possess. The area requirements are minimal. As a rough comparison, the combined area requirement of the major liquid processing units in a P-C system is roughly 2 sq ft/1000 gal/day (0.05 m^2/m^3/day) capacity compared to values of 6 sq ft/1000 gal/day (0.15 m^2/m^3/day) capacity for conventional activated sludge and 12 sq ft/1000 gal/day (0.30 m^2/m^3/day) capacity for extended aeration and low-rate trickling filters. Since the efficiency of the processes depend upon the laws of physics and chemistry and not upon the well-being of a huge population of living organisms with various environmental requirements, the P-C systems should perform in a more reliable manner. Operational flexibility should allow more precise process control than is possible with the biological systems. P-C processes remove many materials which are toxic to biological systems, and are, in general, unaffected by those toxicants not removed. Removals of phosphorus, refractory organics and metals are greater than those obtained by biological systems. And finally, the effectiveness of P-C treatment is not materially diminished by low wastewater temperatures.

From the foregoing, however, it should not be assumed that physical-chemical treatment is universally applicable. The concentration and adsorbability of soluble organics determine whether activated carbon treatment is applicable. The higher the concentration of organics, the more carbon will be required and the more costly the process becomes. Certain organic material, especially water soluble, low molecular weight organics, are poorly or not at all adsorbed. Thus, physical-chemical treatment would be unsuitable for treatment of wastes containing a high proportion of non-adsorbable materials. The basic processes of clarification and carbon do not remove ammonia nitrogen, although high removals of organic nitrogen are obtained. Physical-chemical treatment thus must be considered as an additional option when a wastewater treatment system is being planned.

PERFORMANCE OF PHYSICAL-CHEMICAL SYSTEMS

At present time, performance data from full-scale operating plants are meager, although such information should be available as plants come onstream. Performance data have, however, been accumulated over the past several years on fairly large (~50,000 gal/day [190 m^3/day]) pilot plant systems (2, 13, 16, 17).

Typical effluent quality from a physical-chemical system treating degritted raw wastewater is shown in Table 6 below. The systems consisted of chemical clarification and granular activated carbon operating with or without a granular media filter.

The range in product quality shown in the Table not only reflects the usual expected variation, but also suggests the flexibility that is inherent in the treatment system. As an illustration, organic product quality – COD, BOD– can be allowed to vary over a considerable range simply by operating the carbon adsorption contactors for longer periods thus decreasing the regeneration frequency and concurrently the cost.

TABLE 6. EFFLUENT QUALITY FROM PHYSICAL-CHEMICAL SYSTEMS

Parameter	Concentration Range – mg/l
Suspended Solids	2 - 10
BOD_5	5 - 15
COD	10 - 25
Phosphorus – P	0.2 - 1.0
Color – Units	5 - 10
Turbidity – JTU	<10

Very high product quality is obtainable when physical-chemical systems treat biological effluents. The product, in many instances, is suitable for a variety of reuse purposes including use as supplement to potable water source. Product quality anticipated from this type of system is illustrated in Table 7.

TABLE 7. EFFLUENT QUALITY FROM TERTIARY PHYSICAL-CHEMICAL SYSTEMS

Parameter	Concentration – mg/l
Suspended Solids	< 1.
BOD_5	≈ 1.
TOC	1 - 2
COD	<10
Total Nitrogen – N	2.0
Total Phosphorus – P	0.1
Metals	meet drinking water standards
Coliform Bacteria, MPN/100 ml	< 2.2
Fecal Coliform Bacteria, MPN/100 ml	< 2.2
Virus	0

Actual performance of a physical-chemical pilot plant system operated at Pomona, California, for an extended time–27 months–is shown in Table 8 (17). Also shown are the engineering parameters of each of the two major unit processes–chemical clarification and carbon adsorption systems.

SUMMARY

Research during the past decade has provided the design engineer with an array of unit processes which provide, as never before, a capability to treat municipal wastewater to almost any product quality. Increasingly, these unit processes are being used alone or combined with biological processes to satisfy the needs of any specific plant. The number of possible combinations is large. All that is needed for a successful operation is the ingenuity of the design engineer.

TABLE 8. PHYSICAL-CHEMICAL PILOT PLANT POMONA, CALIFORNIA

Parameter	Raw Sewage	Clarifier Effl.	Carbon Effl.
TCOD, mg/l	321	96	19
DCOD, mg/l	49	49	14
SS, mg/l	199	28	7
Turbidity, mg/l		23	6
BOD_5, mg/l		36	8
Color, Units		20	8
P, mg/l	11.1	1.3	0.9
NO_3-N, mg/l		0.9	1.3
pH	7.7	6.8	6.8

Clarifier
- Flow – 60 gal/min (3.8 l/sec) constant
- Overflow rate – 1180 gal/day/sq ft (48 cu m/day/sq/m)
- Weir loading – 10 gal/min/ft (2 l/sec/m)
- Detention time – 84 min.
- Alum dose – 25 mg Al/l
- Polymer dose – 0.3 mg/l anionic
- Sludge Production – 2000 lb/mil gal (250 mg/l)

Granular Carbon
- Flow – 50 gal/min (3.2 l/sec) constant
- Hydraulic loading – 4 gal/min/sq ft (10 cu m/hr/sq m)
- Contactor type – single-stage, packed-bed downflow
- Carbon size – 8 x 30 mesh (3 x 0.8 mm)
- Empty bed contact time – 30 min.
- Sodium nitrate dose – 33 $NaNO_3$/l
- lst cycle carbon loading – 3.5 g TCOD removed /g carbon (1.5 g DCOD/g)
- lst cycle carbon utilization rate – 173 lb/mil gal (21 mg/l)

Note:

Carbon column ran 18 months (1st cycle) prior to regeneration and was not exhausted. Three regeneration runs were conducted in order to obtain regeneration data. Performance data shown above is average data over entire 27-month operation.

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STUDIES ON WASTEWATER TREATMENT WITH FLOCCULANTS APPLICATION.

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(VNII VODGEO)

The industry growth and the rise of populated areas accomplishment is attended with the formation of a great number of wastes, which result in an environment pollution. In this connection great attention is paid nowadays on environment control improvement, including prevention of water sources pollution. Various chemicals (oil products, acids, carbohydrates, alkalis, cyanides, sugars, pesticides, detergents etc.) flowing together with sewage break the natural processes taking place in water reservoirs sometimes cause failure of water supply of populated area and enterprised. Rendering such substances harmless at the mechanical and biomechanical treatment stations presents considerable pitfalls, and demands large capital and operating costs. Besides, the removal effect of some contaminations, for example oil products, heavy metals, organic compounds, biochemically difficult oxidizable biogenous substances, is not in accord with sanitary standards and causes the necessity of the subsequent post treatment.

At the same time requirements to the quality of treated sewages disposed into the reservoirs or directed to the reused systems are ever increasing.

It should be also noted that structures of mechanical and biological treatment, used in most cases, have the considerable sizes, treatment process in which requires prolonged time and process control in these conditions presents some difficulties.

So, currently, along with the successes achieved in the field of mechanical and biochemical treatment other possibilities of rising efficiency of rendering contaminations in sewage harmless are being searched. The combined use of mechanical, physical and chemical, chemical and biological sewage treatment is one of such trends.

Such treatment schemes find ever expanding application in practice of rendering industrial and domestic sewage harmless. The experience of mentioned stations use shows that the performance of physical and chemical, and biochemical treatment structures gives the possibility to increase the efficiency of contaminations removal, significantly reduce the time of liquid treatment and etc.

In some cases, by application of mechanical, and physical and chemical treatment only, the standards for the treated effluents, intended for the reused purposes may be achieved. The ever increasing attention to the process of physical and chemical treatment derives also from the fact, that they have a number of advantages, for example, in comparison with biological treatment, physical and chemical treatment structures require less areas for their location, there is a possibility to remove substances, toxic for active sludge microorganisms, difficult oxidizable and biogenous contaminations and to make the treatment process fully automatic and etc.

New highly efficient flocculants formation aids in successful use of chemical process in physical and chemical treatment while neutralizating industrial and domestic wastewaters.

As a rule their use in small doses in water treatment process makes it possible to get less quantity of sediment and to intensify all the technological processes of the industrial effluents.

However, at present, the majority of the present physical and chemical treatment structures still use mineral coagulants–aluminium salts, ferrum salts and lime, which have some significant disadvantages: large chemical doze, small strength of flock formation, low rate of hydrolysis large sludge volume, difficulties related to dewatering and utilizing of large quantities of sludges.

The studies show that providing water supply industry with highly efficient flocculants makes it possible to increase more the efficiency of physical and chemical treatment structures.

This paper presents the results of studies on wastewater treatment by applying flocculants and their combinations with mineral coagulants. Experiments were carried out on effluents of such industry fields as chemical, petroleum chemical and paper and pulp.

Separation of solid phase (flock) and liquid was performed by settling in cylinders for an hour or two and filtering through paper filter, model filter with the sand medium, compression flotation in laboratory installation with flotation camera of 100 mm diameter and 1500 mm height.

As the majority of industrial effluent contaminations has the negative charge, the studying of water soluble cationic flocculants, macroion of which is positively charged, is of particular interest. Such flocculants are able to cause natural coagulation of negatively charged particles.

There are also given the results, obtained by a number of scientists.

The greatest emphasis in our work is placed on oil contained sewage treatment studying, because of its complex composition and substantial quantity of organic substances with the difficulty oxydized ones among them.

So, in order to study the high treatment rate of oil contained sewage, the use of highly molecular synthetic flocculants, both independently and together with

TABLE I

Flocculants' marks	Vinylpyridines	Alkylating agent	Viscosity character / / delitre/ /g	M 10^{-6}	Exchange volume mg-equiv/ /g
1	2	3	4	5	6
HPS-46	4-vinylpyridine	CH_3	0.75	–	3.94
HPS-47	–"–	C_2H_5	0.76	–	3.23
HPS-48	–"–	C_3H_7	0.70	–	3.47
HPS-49	–"–	C_4H_9	0.20	–	3.48
HPS-411	–"–	C_2H_5Br	0.78	–	4.05
HPS-11	2-methyl-5 vinyl piridine	C_2H_5Br	0.4	0.112	4.44
	–"–	–"–	2.26	0.726	4.2
	–"–	–"–	4.0	1.26	4.16
	–"–	–"–	9.4	3.24	3.80
HPS-7	–"–	C_2H_5	0.4	–	3.5

mineral coagulants–aluminium sulphate, hydrolysis of which occurrs with a rather high rate at pH 6.5 - 75, was investigated.

Highly basic water soluble polyelectrolites of HPS serie (highly molecular pyridine salts on vinylpyridine base). Characteristics of the mentioned polyelectrolites are presented in Table 1.

In this case from sewage with COD = 558 mg0_2/1, 64 mg/1 of suspended solids and 40.8 mg/1 of oil products, contaminations are removed by 80%, 93.2% and 73% respectively.

Note: Molecular mass of polyelectrolites HPS-II was calculated from the following formula

$$[\eta] = 7.16^{\circ}10^{-6}M^{\circ}94$$

In combined raw sewage treatment with the aluminium sulphate and flocculants HPS-46, 47, 48, 49 with the subsequent settling during two hours, it was found that HPS-47 application was the most efficient (Table 2).

Table 2 Influence of flocculant type on treatment efficiency of petroleum contained wastewaters with coagulation and settling. (2 hours)

Flocculant description	Dose mg/1		treatment efficiency, %		
	$Al_2(SO_4)_3$	of flocculant	COD	suspended solids	oil product
1	2	3	4	5	6
HPS-46	48	2.0	23.1	90.8	-
HPS-47	48	2.0	80	93.2	73
	96	2.0	33.2	96.5	88
HPS-48	48	2.0	70	95.4	-
	96	2.0	33.2	91.5	70.5
HPS-49	48	2.0	19.7	86.0	-
	48	0	13.1	90.5	69
	96	0	26.6	95.5	77.5

It should be emphasized that in the same conditions but without flocculant, the COD value decreases only by 13.1%. It is supposed, that high treatment efficiency is achieved by interaction of flocculant with contaminations found in the water not only in emulsifiable but in dissolved condition.

From the mentioned materials it is apparent that the rate of treatment from suspended solids and oil products by applying HPS-47 is also increased. Doubling the coagulants dose in this condition, in fact, does not change the treatment efficiency from the suspended solids, yet causes the COD increase from 20 to 70% in treated residual water.

So application of aluminium sulphate and flocculant with 50 mg/1 and 2 mg/1 respectively concentrations looks more promising in comparison with the usually used at oil refineries doses of one coagulant, equaled to 100-150 mg/1.

The possibility of water treatment by the use of flocculants only was also studied. The preliminary experiments demonstrated low efficiency of 4 vinylpyridine based flocculants in settling process of two hours duration. Consequently, flocculated flocks removal by filtering was studied.

The results obtained in wastewater treatment process, at COD-52 mg/1 and 58 mg/1 of petroleum products concentration, and treated with 10 mhmg/1 polyelectrolyte, are given in Table 3.

It is apparent from the obtained data analyses that 2 methyl-5 vinylpyridine and 4 vinylpyridine based polyelectrolytes alkylated with (ethyl bromide and ethyl iodide (HPS-47, HPS-411, HPS-11) were found to be more efficient from all polymers flocculants in flocculation and filtration process. These flocculants application makes it possible to reduce COD value by 87.5% and oil concentration by 93.4%. Molecular weight increase of flocculant HPS-11 from 112000 to 726000 results in COD removal by 50%. This is due to the fact that macromolecule size increase causes bonding of the large number of colloid particles to the one polymeride macromolecule forming therewith large flocks.

TABLE 3. TREATMENT EFFICIENCY WHEN FLOCCULATION WITH FILTRATION USED.

Flocculant type	Treatment efficiency, %% Petroleum Products	COD
HPS-46	91.0	14.1
HPS-47	88.4	87.5
HPS-48	93.4	37.9
HPS-19	91	-
HPS-411	91	87.5
HPS-7	88.4	65.6
HPS-11 M∿s=1[illegible]2000	95.4	38.2
HPS-11 M∿s=27[illegible]6000	92.5	87.5

In an effort to determine the influence of the flocculant molecular weight on treatment process, experiments were performed on coagulated wastewater treatment by means of settling and compression flotation.

Fig. 1 presents gained results. The displayed data demonstrate that removal efficiency rises with the increase of polyelectrolytes molecular weight. At the same time flotation during 10 minute provides better suspended solids removal in comparison with settling for an hour. So flotation treatment of oil contained sewages pretreated with polyelectrolyte HPS-11 ($M=3.24.10^{-6}$) and containing 57 and 75 mg/1 of suspended solids gave their removal to the residual concentration 4.0 and 9.0 respectively that constitutes 80.5% and 93%.

Wastewater COD in the treatment process decreases by 70.6 and 75.6%, oil products– by 75%. (C_0 = 36 mg/1).

From other types of polyelectrolites VA-2 (polystyrene based quarternary ammonium salt), P EI (polyethyleneimine), cationic polyacrilamide. The comparison analysis of treatment rate of preflocculated wastewaters by settling and filtration method, shows, that P EI (molecular weight = 80000) is the most efficient. Optimum dose of P EI determined by experimental coagulating method averaged 5 mg/1.

Results obtained during oil contained sewage treatment with flocculants, are given in Table 4.

In an effort to intensify the suspension removal from water, treated with flocculant PEI (5 mg/1 dose), sewage treatment by compressure flotation method was conducted. The performed experiments demonstrated considerable decrease of contaminations amounts in sewage with 21 - 36.7 mg/1 suspended solids, 484-600 mg 0_2/1 COD 40.7-172 mg/1 ether extracted ones, after treatment by pressure flotation and cationic polyelectrolites preliminary introduced into sewage.

TABLE 4

Indices	Sewage composition After oil separator	After physical and chemical treatment C -5mg/1 PEI
1	2	3
PH	7.1 – 7.7	7.1 – 7.8
COD mg/1	580 – 1300	270 – 660
BOD mg 0_2/1	98.0 – 130	15.0 – 24.5
Suspended solids mg/1	87.6 – 133	2.1 – 4.6
K – P mg/1	9.55 – 155.8	0.75 – 5.4
Volatile phenols with vapour, mg/1	0.65 – 9.6	0.6 – 8.9
Non ionogenous detergents, mg/1	6.5 – 16.0	5.5 – 14.5
Chlorides	2950 – 5700	–
PEI mg/1	–	0.003 – 0.07

Thus, suspended solids concentration reduces by 72-95%, etherextracted substances by – 89 – 91% and COD value – by 36 – 56%.

It is a matter of general experience, that reagent introducing place, plays a leading role in sewage treatment by flotation. In most cases, for removal of the major portion of contaminations, petroleum products for example, the chemical supply into saturator is efficient and in post treatment process of biologically treated sewages; when easily broken flocks are removed, coagulant is supplied to a flotation chamber.

It turned out in this case that polyethylene introducing place in flotation process has no practical influence on treatment efficiency.

The duration of water presence in flotator is one of the factors responsible for process economy.

The study of influence of pressure flotation efficiency on time, revealed that the bulk of contaminations amount is removed in 5 minutes and in 10 minutes the process is over. The following water presence in flotation chamber leads to the foamy layer damage which causes the water pollution again.

In ballast and industrial sewage treatment of petroleum transshipping reserves, the efficiency use of some flocculants of cationic, anionic, and non ionic character was studied.

Among cationic polyelectrolites polyethyleneimin, poly–1.2 dymethyl–5 vinylpirydine–methyl sulphate (PPS), poly–1 ethyl–2 methyl–5 vinylpyridine-bromide (HPS-11), polyelectrolites of VA serie: VA-212, VA-112, VA-102 were tested. Among nonionogenous and anionic flocculants metas (copolymeride of metacrylamide and metacrylitic acid), polyacrylamide and its derivatives: PAA-H and RAA-R were used.

The comparative evaluation of mentioned polyelectrolites efficiency was made on the basis of the experimental sewage clarification for two hours in one litre cylinders at various dose presence of studied substances.

When studying the simultaneous effect of aluminium sulphate with anionic and nonionic flocculants on treatment rate of ballast and industrial sewage it was revealed that the highest treatment efficiency is achieved by the use of polyacrylamide (C =1.0 mg/1) for ballast waters and metas (c = 2 mg/1) for industrial waters. Aluminium sulphate concentration constitutes 8 mg/1 (by aluminium ione). Thus at optimum chemicals doses after an hour settling of ballast and industrial sewage of oil transshipping reserves, suspended solids concentration reduces by 68 and 98%, and sewage COD–by 75% and 30% respectively.

In order to achieve the same treatment rate after an hour settling at sewage treatment with aluminium sulphate, chemicals dose constitutes 25-32 mg/1 (by ione Al^{3+}).

Ballast and industrial sewage treatment with cationic flocculant and subsequent sewage settling, makes it possible to evaluate the influence of flocculant nature and its dose on treatment efficiency.

Fig. 2, 3 give the curves of suspended solids decrease and ballast industrial sewage at settling. From the obtained data it is clear that the most efficient were flocculants VA-112, PPS and H C = 11 (mol. weight = 726000, the use of which at 5 mg/l amount allows to reduce suspended solids concentration by 75-83.5% and COD–by 40-50%.

At flocculation and settling of industrial sewage of oil transshipping reserves, best results were obtained by the use of PPS strong basic polyelectrolite of 3 mg/l concentration, for example PPS flocculant application allows to reduce suspended solids concentration to 22 mg/l (with initial =108 mg/l), COD - with initial = 170 mg/l.

In order to intensify the process of flocculated flocks separation and sewage clarification, treatment by compressure flotation method was also used, as a result of conducted studies it was found that high treatment effluency may be achieved either by application of anionic and nonionic type flocculant, or by independent use of cationic flocculants. Thus, flotation treatment of ballast sewages, treated with aluminium sulphate (C = 8 mg/l by A ione) and metas (C = 2 mg/l) gives the possibility to reduce oil concentration to 1.7 mg/l (with the initial = 45 mg/l). The use of one coagulant (C = 8 mg/l) allows to reduce oil products concentration only to 5 mg/l.

Among cationic type flocculants at flotation treatment PPS–is the most efficient. So, at treatment with the mentioned flocculant of 3 mg/l concentration, the suspended solids amount in sewage decreases from 30.5 to 11.0 mg/l, and petroleum products – from 7.6 to 2 mg/l.

Investigation of municipal sewage treatment by the use of PEI, carried out at the Scientific Research Institute of municipal water supply and sewage treatment of the Academy of municipal management named after Pamphilov, demostrated that PEI allows to remove from sewage substances, being in the water both in colloid and dissolved condition (dye–stuffs, naphthenic acids and humic substances, ions of transitive metals). The results of one serie of experiments, when precoagulated water was subjected to settling and filtering, are given in Table 5. Optimum PEI dose, determined by the experimental coagulation method, ranges from 2 to 80 mg/l and averages 10 mg/l. The increase of dose higher than optimum one leads to the decrease of sewage treatment efficiency.

As it was stated earlier, the available treatment methods (mechanical and biochemical) do not allow complete removal of difficulty oxidizable substances from sewage; acid type dye-stuffs in particular.

Regarding this, high molecular flocculant application for this purpose is of great practical interest.

Studies carried out by the Moscow chemical and technological Institute named after Mendeleyev in cooperation with the Central Scientific Research Institute of wool, demonstrated that the use of polyelectrolites of serie HPS, results in a high degree of sewage treatment from dye-stuffs.

Best results were got by using HPS-11 with 1.260000 molecular weight, as a precipitator. Polyelectrolite molecular weight decrease is accompanied by the increase of polymer recipitator dose. Besides, it should be emphasized that dependence degree of dye-stuffs removal from water solutions reaches its maximum at increase of the polymeric precipitation dose.

Ionogenous group presence both in dye-stuffs and polyelectrolites molecules, gives the reason to expect that dye-stuffs settling takes place as a result of chemical interaction of these functional groups, condition of which (dissociation rate) has the main influence on flocculant settling ability.

The increase of polyelectrolite molecular weight results in viscosity increase and consequently–in increase of size and efficient charge of polyelectrolite macromolecule. Settling ability of flocculant BBC changes is also in the same way.

Optimum flocculant dose depends on dye-stuffs concentration and ranges from 2 to 20 mg/l and averages 10 mg/l. The rate of sewage treatment ranges from 75 to 100% depending on dye-stuffs' nature.

Correlating of the experimental results for dye-stuffs of different types (polyelectrolite dose, settling rate) points to the fact that dye-stuff molecules react to some elementary flocculant links.

Sewage post treatment with chemical application.

Chemical treatment of sewage, biologically treated with mineral coagulants with the subsequent separation

Table 5

Contamination type or factor, charactorising water quality	Water, flowing to treatment	Municipal sewage			
		Coagulated mg/l		% of treatment	
		settled	filtered	at settling	at settling and filtering
1	2	3	4	5	6
BOD	87-139	40-61	16-24	51.0	81.0
COD	200-435	99-191	58-108	53.0	73.2
Suspended solids	120-168	26-61	0.8-37	76.7	97.8
Protein substances	79-417	74-98	6.9-48	69.3	86.5
Oil products	10-40	-	0 - 0.17	-	99.8
Detergents	3.1-5.8	0.8-3.6	0.9-1.6	-	71.3
Alizarine	0.84	0.64	0.1	2.38	88.0
Indigo carmine	0.63	0.35	0.15	44.4	76.2
P_2O_5	20-31.5	12-25.5	11-15	38.0	61.6
Cu^2	2.3-4.0	0.5-1.6	0.2-0.5	68.0	91.1
Cr^2	7.7-10.3	1.7-3.4	0.6-1.9	48.6	79-O
Ammonia nytrogen	8-32	8-28	7.5-28	5.0	8.3

of coagulated contaminations by pressure flotation method is one of the efficient methods of post treatment. Investigations were conducted on biologically treated sewages of oil refinery (OR), integrated pulp and paper (IPPM) and chemical mills (ICM).

Treated water characteristics are given in Table 6.

Table 6

Item	O R	ICM	IP.PM
pH	7.1	7.0	7.0
Suspended solids mg/l	8.0-20.0	25.0	20-100
Ethersoluble mg/l	14-20	–	–
Sulphides mg/l	34	–	–
Chlorides mg/l	610	–	–
Phosphate, mg/l	2	–	1.8
Ammonia nitrogen mg/l	3.5	5.2	
Nitrite nitrogen mg/l	2.5	0.22	
Nitrate nitrogen mg/l	12.0	46.7	
Phenol mg/l	0.35	–	–
Saltcontent, mg/l	840	–	–
COD mg/l 0_2	90-200	40	600
BOD full, mg/l 0_2	75	–	–
BOD_5 mg/l 0_2	7.0	3.0	20-50
Dissolved oxygen, mg/l 0_2	2.9	–	3.0

As a result of investigations carried out on coagulation of sewages intergrated chemical and oil refinery mills with aluminium sulphate, and subsequent treatment by pressure flotation method, it was revealed, that coagulant application at doses from 2 to 10 mg/l is accompanied by the increase of sewage treatment rate. Thus, at aluminium sulphate dose of 10 mg/l, concentration of suspended solids reduces to 1.7 mg/l (with the initial = 9.0 mg/l; ethersolubles one–to 6.7 mg/l (with the initial = 16.7 mg/l) COD value–to 84 mg/l (with the initial = 188 mg/l).

Studies on posttreatment sewages of the pulp and paper industry by pressure flotation method, were conducted both with coagulant application and without it. Aluminium sulphate with concentration ranging from 2 to 20 mg/l (by ion A) was used as a coagulant.

The optimum sulphate aluminium concentration, consisting 10 mg/l, provides suspended solids removal by 80-90%, phosphorus ones–by more than 50%.

BOD_5 and COD values therewith reduces by 40% and 70% respectively. At the same time water saturation with oxygen, the contents of which encreases 2-3 - fold after a ten minutes flotation, takes place.

It may be said in conclusion, that in all cases flocculant application for treatment of sewages of different composition is accompanied by the increase of treatment rate. At present, polyelectrolites application in sewage technology is often in particular need and non-replaceable and sometimes it is more efficient despite the high cost.

THE OPERATION OF THE PHYSICAL-CHEMICAL PLANT AT ROSEMOUNT, MINNESOTA

Dr. Robert Polta

INTRODUCTION

The Metropolitan Sewer Board of the Twin Cities Area was formed in 1969. In 1970 the MSB acquired the 33 wastewater treatment facilities and 320 miles of interceptor in the 7 county metropolitan area. Of the 33 plants acquired only 4 produced treated effluents in compliance with applicable water quality standards. Twelve plants have been closed to date and several others have been upgraded. Three new treatment facilities have been put into service since 1972–one being the Rosemount advanced wastewater treatment plant (AWTP).

The original Rosemount treatment facility consisted of a high rate trickling filter plant which discharged to an effluent seepage pond from which the effluent escaped by percolation and evaporation. No other outlet was available for the effluent at that site and the seepage pond was operating at capacity. Thus it was not possible to expand the plant to meet the increasing hydraulic loading.

The new plant was to discharge to Spring Lake which is part of the Mississippi River. At that time however studies were being made to determine the feasibility of separating the lake from the Mississippi River and designating it for recreational use. The evaluation of the water quality standards and their applicability to receiving waters of limited dilution capacity led to the adoption of the following effluent quality limits for design criteria:

BOD	– 10 mg/l
Suspended Solids	– 10 mg/l
Total Phosphorus	– 1 mg/l

Ammonia Nitrogen – 1 mg/l
Total Coliform Organisms – 1000 MPN/100 ml

Several design alternatives were evaluated for a design flow of 0.6 MGD. Estimated owning and operating costs indicated that a physical-chemical treatment facility would be most cost efficient. It was also recognized that the use of these new treatment processes would serve to fully evaluate the feasibility, economics and application of individual unit processes for future treatment plant construction elsewhere.

The decision was made in 1971 to build the Rosemount AWTP. The gate opened November 20, 1973 and the facility has been in operation since that time.

PLANT DESCRIPTION

General

The plant is composed of process units totally enclosed in a 15,000 sq. ft. steel building. After metering and coarse screening the flow is pumped to one or two parallel process trains each with a design capacity of 300,000 gal/day, Figure 1. The essential treatment units in each process train are presented in Table 1 in the order in which they appear in the plant.

TABLE 1
ROSEMOUNT AWTP – ON-LINE PROCESSES

Unit	Function
Suspended solids contact clarifier (1)	BOD, suspended solids and phosphorus removal
Dual media filters (2)	suspended solids removal
Granular activated carbon colums (3)	soluble organic removal
Dual media filters (2)	suspended solids removal
Ion exchange columns (clinoptilolite)	ammonia nitrogen removal

Considerable operational flexibility exists within each train. The first stage filters (DMF_1) can be bypassed. The carbon columns may be operated in several modes. The second stage filters (DMF_2) may also be bypassed.

The flow from the two trains is mixed prior to chlorination and discharged to the Mississippi River (Spring Lake) through a forcemain approximately one and one half miles long.

The support or off-line processes at the plant include chemical feed systems, activated carbon transfer and regeneration systems and a zeolite regeneration system.

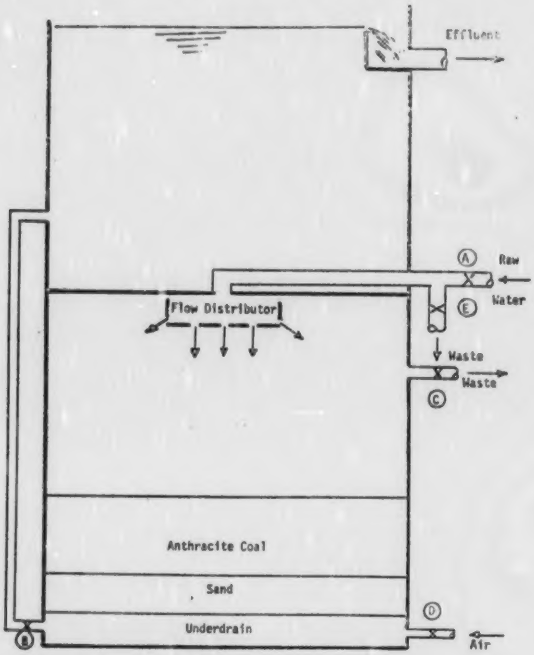
ON LINE PROCESSES

Clarification

A suspended solids contact clarifier is the first unit in each process train. The units are 25 feet in diameter and have a side water depth of approximately 13 feet–see Figure 2. At design flow (208 gal per min. per unit) the surface settling rate is 0.5 gal per min per square foot and the detention time is approximately 3 hours and 45 minutes.

Each unit is equipped with a skimmer and grease box as well as a rotating sludge plow. A variable speed turbine type mixer is used to provide turbulence for mixing the chemicals with the sewage flow. This turbine also affects sludge recycle through the draft tube. Sludge is removed from the clarifier on a flow proportional basis, by gravity, and discharged to a holding tank. The sludge is currently disposed of by hauling to another MWCC facility or by subsurface injection on site.

The clarifier overflow is collected and discharged to a weir box where sulfuric acid can be added for pH control as required. The overflow rate is determined at this point to allow for flow proportional chemical additions in the clarifier.



DUAL MEDIA FILTER
Rosemount AWTP
Figure 3.

Filtration

The two primary and two secondary filters per train are essentially identical. The backwash water storage tank is located directly above the filter box as illustrated in Figure 3. Each filter box is 8 feet in diameter providing for loading rates of 2 gal per min per square foot at design flow. The loading rate doubles when one filter of a pair is taken out of service for backwash. The filter media consists of approximately 24 inches of anthracite coal with an effective size of 1.1mm and 12 inches of sand with an effective size of 0.45 mm.

During normal operation the raw water enters valve (A) and passes through the flow distributor and down through the filtration media and underdrains, through valve (B), up through the backwash storage compartment and over the discharge weir. When backwash is initiated valves (A) and (B) close and valve (C) opens to drain down the filter box to that level. After this is accomplished valve (C) closes and valve (E) opens and valve (D) opens to allow air to pass up and scour the media. Valve (D) then closes and valve (B) opens to provide an upflow expanded bed wash. After backwash, valve (E) closes and valve (A) opens. The filter is then ready for service.

The available head allows for backwash rates of approximately 15 gal per min per square foot. The air scour rate is approximately 5 cubic feet per square foot per minute. Backwash is presently initiated manually although a program timer is available for automatic initiation.

Carbon Adsorption

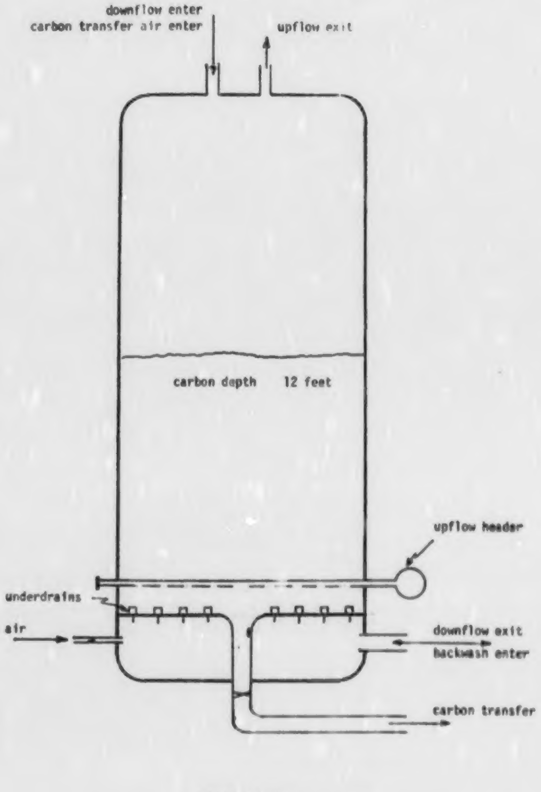
Each of the three carbon columns per train is 8 feet in diameter and approximately 27 feet high–See Figure 4. A nominal depth of 12 feet of granular activated carbon (Westvaco 12 x 40 mesh) is maintained in each column. The piping and valve arrangement (32 air activated valves per carbon column train) allows considerable flexibility in terms of operating modes. Any 2 of the 3 columns may be operated in the following modes: series upflow, series downflow, primary upflow and secondary downflow and parallel downflow. Series upflow and series downflow have been the primary operating modes to date.

The carbon columns are backwashed on a routine basis to remove debris and to limit the accumulation of biomass in the carbon bed. The procedure includes a 30 minute air scour and a 15 minute backwash at a rate of 12 gal per square foot per minute.

When the desired organic removals can not longer be maintained across the carbon column, one of the columns is taken out of service and replaced with a column containing regenerated carbon. The spent carbon is transported to the regeneration facility by an air aided hydraulic transfer. Water is pumped through the backwash entrance and air supplied to the top of the column at 12 psi as the valve on the carbon transfer line is opened. The carbon slurry is thus forced through the transfer line and discharged to the spent carbon holding tank. The 600 cubic feet of carbon can be transferred in approximately 20 minutes.

Ion Exchange

The ion exchange columns are pressure vessels 8 feet in diameter and, approximately 14 feet high. Each column contains a 6 foot depth of the natural zeolite clinoptilolite (20 x 50 mesh) supported on gravel packing and plastic strainers. The plant flow passes down through two zeolite beds in series. When the NH_3-N level in the effluent of the second column reaches a predetermined level the primary column is taken out of service for regeneration. The secondary column is moved up to the primary position and a regenerated column is placed in the secondary position.



CARBON COLUMNS

Rosemount AWTP

Figure 4

OFF LINE PROCESSES

Chemical Feed Systems

Lime

Lime slurry is used to maintain an elevated pH in the clarifier when required. The lime delivery system as illustrated in Figure 5 consists of a lime storage silo with capacity for approximately 30 tons hydrated lime, a slurry mixing tank with a capacity of about 1650 gallons, slurry transfer pump, a slurry storage tank of about 8000 gallons capacity and four, variable stroke, diaphram chemical feed pumps. The lime slurry concentration is maintained at approximately 2.5%. The slurry feed pumps have a maximum capacity of 5 gallons per minute each and are used to maintain flow proportional lime feed.

Ferric Chloride

Liquid ferric chloride (approximately 40% $FeCl_3$) is delivered to the plant and stored in a 6500 gallon fiberglass tank. The ferric chloride is used as a coagulant in the clarifier. Four, variable stroke, diaphram chemical feed pumps deliver the ferric chloride to the clarifiers on a flow proportional basis. The pumps have a capacity of 15 gallons per hour each.

Polymer

An anionic polymer is used as a coagulant aid in the clarifier. The polymer is delivered in liquid form and diluted to a concentration of 0.25% in one of two mixing tanks. Four, variable stroke, diaphram chemical feed pumps feed the solution to the clarifier on a flow portional basis. The pumps have a capacity of 7.5 gallons per hour each.

Chlorine

Chlorine is supplied to the plant in one ton cylinders. Two standard vacuum operated chlorinators with manual rate control are used to deliver chlorine solution to the effluent and at several points in the plant. The plant effluent is served by a unit with a capacity of 100 pounds per day. The in-plant chlorine is supplied by a unit with a capacity of 400 pounds per day.

Activated Carbon Regeneration

The carbon regeneration system is illustrated in Figure 6. Spent carbon is transported to the dewatering tank where gravity drainage reduces the moisture content to appromately 50%. A variable speed screw conveyer then delivers the carbon to a multiple hearth furnace. The four hearth furnace is 54 inches in diameter and is equipped with a wet scrubber and afterburner to control stack emissions. During regeneration the hearth temperatures are maintained in the following ranges:

Hearth	Temp. Range – °F
1	900 to 1050
2	1400 to 1500
3	1550 to 1650
4	1600 to 1700

Steam is injected into hearth number 4 to aid in the regeneration process.

The carbon is quenched as it discharges from the furnace and is transported to a storage tank similar to the on-line carbon columns. Carbon is transferred from the storage tank to one of the on-line columns by the transfer technique previously described.

Zeolite Regeneration

When an ion exchange column is taken out of service and the regeneration process is initiated the sequence is as follows (Figure 7):

(1) The column is backwashed, upflow, at a rate of approximately 8 gallons per square foot per minute.

(2) The hot brine is pumped through heat exchangers 1 and 2 and then the cooler – which protects the ion exchange media against temperatures in excess of 80°F – and up through the media. The spent brine returns through the heat exchangers and is discharged to a storage tank.

(3) After a clean water rinse the ion exchange column is again ready for service.

The spent brine is rejuvenated by the following procedure:

(1) The pH of the spent brine is adjusted to 11.5 and sodium carbonate is added. The $CaCO_3$ and $Mg(OH)_2$ thus formed is allowed to concentrate in the tank bottom and then pumped to the sludge storage tank.

(2) The desludged brine is then pumped through heat exchanger 1 or 2 and discharged to the stripping tower.

(3) Steam is injected into the stripping tower at a rate of approximately one pound per gallon of brine.

(4) The volatile NH_3 along with water vapor are discharged from the top of the tower to an air cooled condenser.

(5) The condensate discharges to a receiver at a concentration of about 1% NH_3-N.

(6) The regenerated brine is pumped from the bottom of the stripping tower through the appropriate heat exchanger and discharged to storage where the salt concentration is adjusted to 1 normal NaCl.

Sulfuric acid and sodium hydroxide are added as required for pH control in the two brine tanks.

PLANT PERFORMANCE

General

The Rosemount AWTP was put into operation in mid November 1973 and since that time has been the only treatment facility serving the City of Rosemount. During the approximately 2 years of operation the facility has produced a high, although somewhat variable, quality effluent as illustrated by the monthly averages presented in Figures 8, 9 and 10.

The initial plant start-up which was supervised by the contractor's representatives lasted approximately 6 weeks. Steady state operating conditions were approached in January 1975. During 1974, however, the plant was plagued by minor equipment failures that were related to design and construction. As a result of these circumstances a number of operating modes were utilized throughout the year as required.

All of the on-line processes were operational in November 1973, however, the two major off-line processes, carbon regeneration and zeolite regeneration, were not. Several attempts were made to regenerate carbon in November 1974 but because of the inability to maintain adequate temperatures in the furnace the carbon was only partially regenerated. The first successful regenerations were made in January 1975. The zeolite regeneration system has been used on a sporadic basis only because of minor problems which were again related to design and construction.

EPA GRANT PERIOD

General

In June, 1973 the U.S. Environmental Protection Agency awarded the Metropolitan Waste Control Commission a research and development grant. The objectives of the grant are to: evaluate the independent physical-chemical treatment facility at Rosemount as a whole, evaluate the individual unit operations and processes, and to determine the costs associated with operation and maintenance. The grant was officially initiated on June 1, 1975. Under the terms of the grant agreement the plant is currently being operated in a number of modes for 8 week periods to determine the affect of plant configuration on performance.

Sampling and Analysis

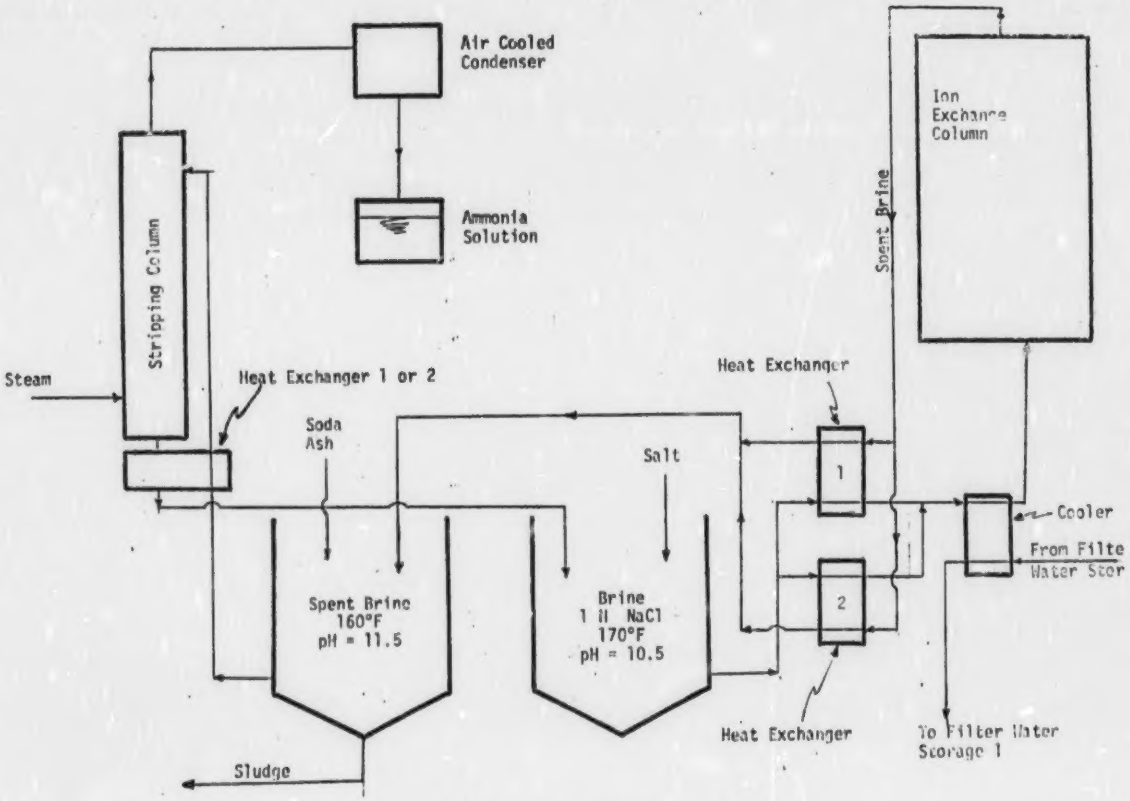
Flow proportional composite samples of each process effluent are collected on a daily basis. The routine analyses and their frequency are presented in Table 2. Other analyses, such as hardness, sulfate, total solids and heavy metals, are made on a less frequent basis as required. The analytical procedures utilized are as described in *Standard Methods* (1) or *Methods for Chemical Analysis of Water and Wastes* (2). The total phosphorus and Kjeldahl nitrogen samples are stored and analyzed on a weekly basis at the MWCC central laboratory using automated chemistry techniques. All other analyses with the exception of heavy metals are performed at the Rosemount laboratory.

TABLE 2

SAMPLE – ANALYSIS FREQUENCY AT ROSEMOUNT AWTP

	Analyses per Week						
	Raw	Clar	DMF_1	GCC	DMF_2	AEC	Eff
BOD – total	3	3	3	3	3	-	3
BOD – filtrable*	3	3	-	3	-	-	3
COD – total	3	3	3	3	3	-	3
COD – filtrable*	3	3	3	3	-	-	3
TOC – total	3	3	3	3	-	-	3
TOC – filtrable*	3	3	3	3	3	3	3
Suspended solids	3	3	3	3	3	3	3
Phosphorus – total	3	3	-	-	-	-	3
total filtrable**	3	3	-	-	-	-	3
total ortho	3	3	-	-	-	-	3
filtrable ortho**	3	3	-	-	-	-	3
Nitrogen – Kjeldahl	3	-	-	-	3	3	3
– ammonia	3	-	-	-	3	3	3
pH	3 3	3	3	3	3	3	3
Alkalinity	3	3	-	-	-	3	3
Chloride	3	3	-	-	-	-	3
Temperature	7	7	7	7	7	7	7
Chlorine residual	-	-	-	-	-	-	7
Dissolved oxygen	-	-	-	-	-	-	7

*giass fiber filter
**0.45 filter


Air Cooled Condenser
Ammonia Solution
Stripping Column
Steam
Heat Exchanger 1 or 2
Soda Ash
Salt
Spent Brine 160°F pH = 11.5
Brine 1 N NaCl 170°F pH = 10.5
Sludge
Ion Exchange Column
Spent Brine
Heat Exchanger
1
2
Heat Exchanger
Cooler
From Filte Water Stor
To Filter Water Storage 1

Zeolite Regeneration System

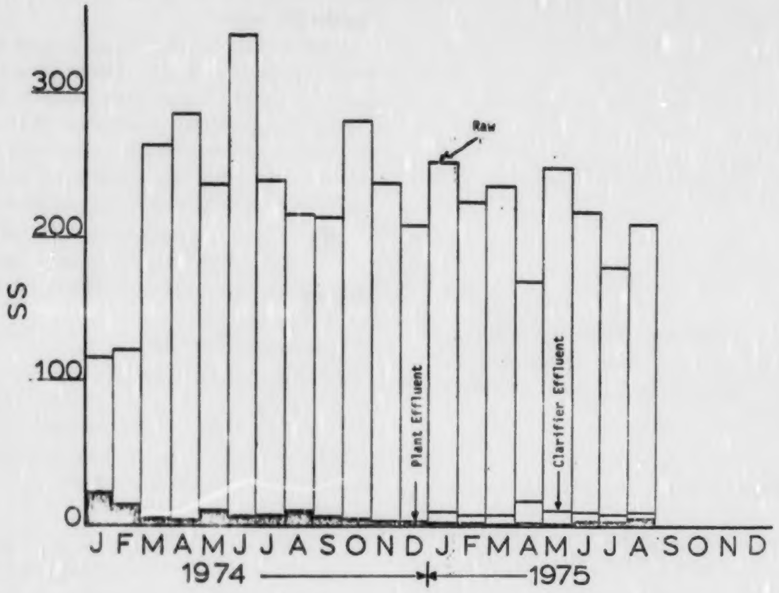
Rosemount AWTP Figure 7

Operating Conditions

General

During the 8 week period June 7, 1975 to August 1, 1975, the plant was operated as follows:

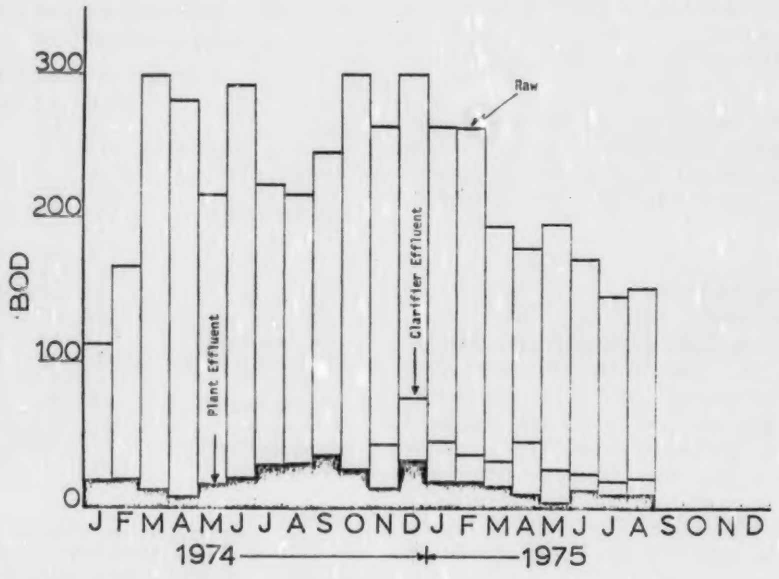
clarifier – lime to pH 10.5, ferric chloride, polymer
DMF_1 – in service
GCC – 2 columns, upflow, series
DMF_2 – in service
AEC – in service when available



MONTHLY AVERAGE SUSPENDED SOLIDS CONCENTRATIONS

Rosemount AWTP

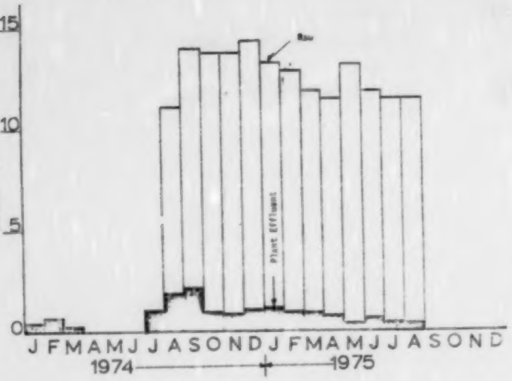
Figure 8



MONTHLY AVERAGE BOD_5 CONCENTRATIONS

Rosemount AWTP

Figure 9



MONTHLY AVERAGE PHOSPHORUS CONCENTRATIONS
Figure 10

During this period the raw flow averaged 221,430 gal per day and the clarifier flow 277,350 gal per day. The sources of recycle flow in the plant include backwash, rinse and sample streams.

Clarifier

The average chemical dosages to the clarifier are tabulated below:

ferric chloride	– 42 mg/l $FeCl_3$ or 14 mg/l Fe
lime	– 560 mg/l $Ca(OH)_2$ or 424 mg/l CaO
polymer-Nalco 677	– 2.9 mg/l
acid	– 20,160 lb H_2SO_4 used

The pH in the mixing zone or draft tube was maintained at 10.5 based on average of 1290 hourly samples. Approximately 400,000 gal of sludge were removed from the clarifier at an average concentration of 4.6%.

Filters

First stage filters number 3 and 4 and second stage filters number 7 and 8 (all in train 2) were used during the 8 week period. Because of the limited capacity to store backwash water in the plant the following schedule was adopted:

filter backwash	– day shift
carbon column backwash	– 3 - 11 shift
zeolite regeneration	– 11 - 7 shift

The filters are backwashed in the morning so that the backwash pit, which is used to store backwash water prior to recycle to the wet well, can be emptied by 1200-1400 hrs. The raw flow to the plant generally starts to increase from a low of about 50 gal per min to 250 gal per min at this time. Additional filter backwashing may be required during the day depending on flow and clarifier performance. The backwash requirements of the four filters for the 8 week period are tabulated below:

Filter No.	No. of Backwash Cycles
3	77
4	77
7	59
8	58

The backwash water requirement amounted to approximately 8.2% of the raw flow.

Carbon Columns

Carbon columns No. 4 and 5 were used during the 8 week test period. Both columns were put in service May 3, 1975, freshly regenerated, in the series, upflow mode. Previous experience illustrated that a backwash frequency of approximately once every 5 to 7 days was sufficient to limit biological growth and the associated problem of hydrogen sulfide generation.

Column No. 4 was backwashed 11 times and No. 5, 10 times during the 8 week period. The backwash water requirement amounted to approximately 1.5% of the raw flow.

Ion Exchange Columns

The ion exchange columns were in service for only 22 days during the 8 week period. The ion exchange columns themselves were available for service but a number of failures in the zeolite regeneration system caused the prolonged down time.

Laboratory Data

The laboratory data summary is presented in Table 3. For the 8 week period the removal efficiencies were:

Suspended Solids	–	98%
BOD	–	93%
Total P	–	95%
NH_3-N	–	21%

TABLE 3
ROSEMOUNT AWTP LABORATORY DATA SUMMARY
(June 7 to August 1, 1975)

	Concentration – mg/l at Sample Location				
	Raw	Clar	DMF_1	GCC	Eff
pH	7.7	7.5	7.6	7.6	7.7
Alkalinity – Ca CO_3	397	79	-	-	75
Hardness – $CaCO_3$	306	201	-	-	187
Chloride	267	314	-	-	351
Suspended Solids	193	9	5	7	4
Turbidity – FTU	-	6	4	6	5
BOD – total	151	21	16	14	11
BOD – filtrable	39	18	-	10	8
COD – total	382	67 6	57	42	36
COD – filtrable	111	47	44	25	25
TOC – total (3)	77	19	16	10	9
TOC – filtrable (3)	32	15	15	8	8
P – Total	11.7	0.6	-	-	0.6
P – total filtrable	8.3	0.4	-	-	0.4
P – total ortho	9.1	0.3	-	-	0.3
P – filtrable ortho	8.0	0.02	- -	-	22
Kjeldahl N	34	-	-	-	22

Notes
(1) temp recorders out of service
(2) DMF_2 and AEC samples out of service
(3) TOC analyzer out of service for 2 weeks

These data again illustrate that the major portion of the removals of suspended solids, BOD and total phosphorus were accomplished in the clarification process.

Organic removal across the carbon columns does not appear encouraging. The effluent BOD of 11 iin Table 3 is slightly higher than the plant design standard. This was partially due to an operational error when a pH controller was inadvertently left in the standby position for a period of about 15 hours. The high pH feed to the carbon columns caused desorption of organics and the effluent BOD rose to 37 and 22 mg/l for two days before returning to below 10 mg/l. The average effluent BOD was 10 mg/l when these two days are discounted.

During the 22 days the ammonia removal system was in service, removals of approximately 60% were accomplished. The low removal efficiencies were apparently caused by failure of the zeolite regeneration system to achieve complete regenerations.

Costs

A separate cost accounting system was set up at the Rosemount AWTP. The plant was divided into 17 cost centers as illustrated in Table 4. Fifteen of the cost centers are defined by physical boundaries. One cost center, Laboratory Service, is defined by function. The last cost center, Indirect Services, is used to identify charges that cannot reasonably be identified with direct plant operation.

During normal operation the three major costs for a plant of this type are chemicals, labor and power. For the 8 week period, June 7 to August 1, 1975, these three categories accounted for 82% of the total operations and maintenance costs, labor – 70%, chemicals – 7%, and power – 5%. A chemical inventory is completed every two weeks and usage determined. All MWCC employees at the plant fill out two time cards on a biweekly basis, the regular time card for pay purposes and a second card to identify hours in the various cost centers. Electric power and fuel usage are metered at the plant entrance but not at the appropriate cost center. Fuel usuage in the appropriate cost centers is readily estimated however and electric power measurement instrumentation is currently being installed on the larger motors.

Labor is by far the major cost factor for the Rosemount AWTP. The operations and maintenance staff consists of 4 operators, 4 assistant operators, 1 pipefitter, 1 electrician, 2 laborers. A full time supervisor directs the operating staff. The plant is staffed by a minimum of two men around the clock. Maintenance is generally performed during the day shift. The staffing requirements of the various cost centers are presented in Table 5. Time spent by the operator at the plant control panel is charged to Indirect Services. The two plant processes that require the most labor time are clarification (cost center 30) and clinoptilolite regeneration (cost center 120). It is quite possible that the distribution of labor time throughout the plant will change considerably when all of the 'bugs' are worked out of the individual processes.

Table 4

COST CENTER	Title and Description
10	PRELIMINARY TREATMENT – plant inlet to discharge to wet well, includes flow measurement, bar screens, raw sampling pump
20	INFLUENT PUMPING STATION – wet well to discharge to SCC
30	CLARIFICATION & PHOSPHORUS REMOVAL – inlet to SCC to weir box on SCC
40	FILTRATION–1 – weir box on SCC to discharge to Storage–1
50	CARBON ADSORPTION – storage–1 to weir box feeding 2nd stage filters
60	FILTRATION–2 – weir box to and including storage–2
70	AMMONIA REMOVAL – ion exchange pumps to discharge from building
80	CHLORINATION – chlorine system for disinfection and odor control
90	EFFLUENT DISPOSAL – building to outfall
100	SLUDGE HANDLING & DISPOSAL – blowdown line (outside SCC) to discharge from truck
110	CARBON REGENERATION – transfer and regeneration
120	CLINOPTILOLITE REGENERATION
130	AMMONIA RECOVERY SYSTEM – condenser and storage tank
140	AMMONIA DISPOSAL – disposition of stored ammonia solution
150	LABORATORY SERVICES – sampling, analysis, monitoring
160	BUILDING & GROUNDS – general systems including water, drain, compressed air, heating, ventilation, cleaning, etc.
170	INDIRECT SERVICES – nondirect labor, plant supervision, project supervision, clerical labor, data processing and other indirect services

Table 5

	Cost Center	Man Hours* (June 7 to Aug 1, 1975)	
10 –	Preliminary Treatment	110	
20 –	Influent Pumping Station	25	
30 –	Clarification & P Removal	540	
40 –	Filtration – 1	58	
50 –	Carbon Adsorption	58	
60 –	Filtration – 2	133	
70 –	Ammonia Removal	32	
80 –	Chlorination	25	
90 –	Effluent Disposal	8	
100 –	Sludge Handling & Disposal	40	
110 –	Carbon Regeneration	24	maintenance w/o operation
120 –	Clinoptilolite Regeneration	521	
130 –	Ammonia Recovery System	85	
140 –	Ammonia Disposal	23	
150 –	Laboratory Service	937	
160 –	Building & Grounds	1,249	
170 –	Indirect Service	970	

* excludes vacation, sick leave, clearical and supervision

The total cost of operating and maintaining the facility for the 8 week period on an actual flow basis was $4.82 per 1,000 gallons. The unit cost is extremely high because the plant capacity and plant flow are low enough to preclude any economy related to size, yet the plant complexity requires full staffing. For plants of moderate size, 5 to 10 MGD, and similar design the unit cost of treatment would be reduced substantially. Although power costs may be proportional to flow, chemical unit costs decrease significantly when carload deliveries are possible. From experience to date it does not apperat that labor requirements will be directly related to flow. If the plant had treated the design flow of 600,000 gal/day for the 8 week period the unit cost of treatment would have been $2.16/100 gal assuming labor cost constant, chemical and power cost directly proportional to flow and other miscellaneous costs constant.

If the capacity and flow to the present facility was increased to 2 MGD by using larger units rather than by adding more units of the present size, the staffing level required probably would not increase by more than 2 or 3 persons. It is obvious that as the plant capacity and flow increase the operation and maintenance man hour requirements per unit of flow decreases thus further decreasing the unit cost of treatment.

SUMMARY

The 0.6 MGD Rosemount AWTP was constructed by the Metropolitan Sewer Board (now Metropolitan Waste Control Commission) to protect potential recreational waters adjacent to the Mississippi River and to evaluate the feasibility and economics of the unit processes employed. The plant was put into service in November 1973 and since that time has been the only treatment facility serving the City of Rosemount. The plant has consistently discharged a high quality effluent.

A demonstration project jointly sponsored by the USEPA and MWCC was initiated in June of 1975. The purpose of the project is to evaluate the unit operation and unit processes utilized at the Rosemount AWTP and to determine the costs associated with the operation and maintenance of the facility.

Operating experience to date illustrates that concentrations of suspended solids, biochemical oxygen demand and total phosphorus can be maintained at levels of 5 mg/1, 10 mg/1 and 1 mg/1 respectively. The ion exchange system used to remove ammonia nitrogen has not yet demonstrated its effectiveness because of numerous problems with the zeolite regeneration system. Although the unit cost of treatment is extremely high at the current facility it is obvious that larger plants of the same general design would operate at considerably lower unit cost because of economic factors related to scale.

REFERENCES

(1) *Standard Methods for the Examination of Water and Wastewater*, 18th ed., APHA, 1971

(2) *Methods for Chemical Analysis of Water and Wastes*, USEPA, 1974

TREATMENT OF CHEMICAL PLANT EFFLUUENTS

M.N. Levchenko

Science and technology advance giving rise to a swift growth of production volume during recent decades makes the problem of pollution control especially serious. Water pollution becomes so high that it appears to be harmful and even disastrous for water reservoirs and has an adverse effect on human's health. This leads to the depletion of river, lake and underground water sources on which the modern water management is based.

Though our country occupies one of the first places in the world as far as fresh water resources is concerned, uneven distribution across the territory of the USSR and a continuous growth of water consumption require a search for ways of economic consumption of fresh water and efficient treatment of effluents.

Chemical industry is one of the largest consumers of water and at the same time it disposes to water reservoirs large amounts of effluents.

In a great majority of chemical processes water is widely used for cooling, material handling and directly in technological processes. At the same time various substances are used at chemical plants as raw materials, intermediates and final products; part of them goes with effluents to water reservoirs.

As a result the chemical industry being no leader in terms of pollution quantities is among the first as far as pollutants range is concerned.

The USSR for a long time has laws strictly limiting pollution with effluents. In recent years the legislative bodies of the USSR and Union republics have adopted still stricter laws relating to pollution control and economical use of natural resources.

For example, in accordance with published in 1975 new "Regulations for surface water Protection from Pollution with effluents" in case of disposal to a water reservoir of several substances with the same permissible concentration and taking into account the pollutants already disposed to the water reservoir from other outlets the sum of concentration ratios ($C_1, C_2 \dots C_n$) of each substance in the water reservoir to the corresponding maximum permissible concentrations (ПДК) should not exceed 1:

$$\frac{C_1}{ПДК_1}+\frac{C_2}{ПДК_2}+\dots+\frac{C_n}{ПДК_n}\le 1$$

Taking into account a large range of pollutants at the chemical plants to be treated it is hardly permissible to dispose even biologically treated effluents to rivers and other water reservoirs.

Until recently a rapid growth of production volume and range of chemicals produced was accompanied by an almost proportional growth of fresh water consumption and effluents amounts. However recent years witnessed a clear trend towards the reduction of fresh water consumption owing to

a) the development and use of new and improved traditional technological processes without effluent formation and with minimum water consumption:

b) maximum use of closed water circulation systems;

c) use in each technological process of local waste water recycling with water treatment at a given process stage and treated water recycling to the process;

d) after-treatment and recycling to the process of effluents including conditionally clean and storm water;

e) a wider use of air cooling instead of water cooling, etc.

Work being done in this direction gives certain positive results. Thus during 1971-75 in spite of appreciable growth of chemical production volume fresh water consumption in the chemical industry as a whole remained at 1970 level.

Today biological treatment is the main type of effluent treatment at the chemical plants. Practically each plant has its biological treatment facilities or sends the effluents to the municipal treatment plant. As a rule biological treatment of industrial effluents is conducted together with the treatment of industrial and municipal sewage. Effluents and sewage ratio varies greatly from 1:3 to 1:10 depending on the amount and type of pollutants in industrial effluents, total amount of sewage, etc. Treatment efficiency is usually 95:98 per cent. In our opinion good prospects exist for after-treatment of biologically treated waste water with its further use for industrial water supply. At Severodonetsk chemical plant it is already for a long time that biologically treated waste water is recycled to the process. Industrial sewage and effluents and municipal sewage are treated together at the biological treatment facilities with the capacity of about 100000 m^3/day. The biological treatment complex includes mechanical treatment of industrial sewage, mechanical treatment of industrial effluents, biological treatment including treatment of residue. After-treatment is carried out in two-step buffer ponds with total surface area of 16 ha. After three-days residence of biologically treated waste water in buffer ponds it is delivered to the industrial water supply filtration plant and then to the additional feeding of water circulation systems. Control of technological processes and treatment degree is carried out by chemical and bacteriological laboratories. According to the analysis the efficiency of biochemical treatment of sewage and effluents amounts to 97-98 per cent and is characterized by the following values: biochemical oxygen demand(БПК) - 4÷12 mg/1, suspended substances - 7-12 mg/1, chlorides - 150 mg/1, sulphates - 100 mg/1, temperature - 20-22°C, pH - 7-8. This water before the delivery to the additional feeding of water circulation systems is treated with ozone in special contact tanks for additional treatment from organic contaminants and for avoiding of biological overgrowing of cooling towers and other parts of water circulation systems.

At the synthetic fibre plant in Chernigov there are biological treatment facilities with the capacity of 80000 m^3/day. They simultaneously treat 68000 m^3/day of municipal sewage and 12000 m^3/day of industrial sewage and effluents. After-treatment is carried out in three-step cascade bioponds with total area of 40 ha. Waste water from biological treatment facilities contains 20-70 mg/1 of suspended substances; БПК$_5$ is 14-18 mg/1. After biological ponds the concentration of suspended substances lowers to 8-20 mg/1, БПК$_5$ to 8-12 mg/1. After the additional treatment in bioponds 12000 m^3/day of waste water are recycled to the process and used for soft water preparation.

Two-step after-treatment of biologically treated waste water is used at nitrogen plant in Dorogobooge. The 1st step-metallic drum filters with filter cloth cell size 0,5x0,5 mm. The 2nd step-sand filters filled with 16-32 mm gravel up to 0,65 m and with 1-2,5 mm quartz sand up to 1,2 m. Filtering rate in sand filters – 6-8 m/hr, filtering time – 12-14 hrs, washing rate – 13-15 1/sec. m^2 washing time – 6-7 min. Washing is carried out with filtered water which is then delivered to the head of treatment facilities. Biologically treated waste water contains up to 50 mg/1 of suspended substances; БПК$_5$ is 15-20 mg/1. After additional treatment the concentration of suspended substances lowers to 5-6 mg/1, БПК$_5$ lowers to 4-5 mg/1 and after mixing with fresh river water the waste water is sent to the water treatment plant and then to the additional feeding of water circulation systems and covering other production requirements.

The experience of the Ministry for Chemical Industry shows sufficient reliability and efficiency of biological treatment of all the sewage and effluents of a chemical plant with their further after-treatment and recycling for industrial water supply. However this is true for ammonia, synthetic fibre and certain other plants where the amount and contamination of industrial waste water are relatively low. For plants producing organic, chloroorganic and other products giving a large amount of waste water and a large range of pollutants the optimum variant in our opinion would be that of a local physico-chemical treatment of industrial waste water in all the water-demanding technological processes using their own water circulation system. Industrial sewage and partially industrial effluents should be treated at all-plant treatment facilities when a local treatment is undesirable.

In the USSR there was developed a complex route for treatment and recycling of waste water of a large production plant without disposal to open water reservoirs. The complex route includes the use of local treatment plants in the production of suspension polystyrene, chlorine and caustic soda by a diaphragm method and acetylene by a thermal oxidative pyrolysis of natural gas. The waste water treated at local plants is recycled to the water circulation system and to the production process.

The waste water unfit for recycling is separated into four types:

– organic polluted
– mineral polluted – above 3 g/1
– mineral polluted – under 3 g/1
sewage,

Mineral-polluted waste water with mineral content above 3 g/1 after treatment (softening, separation of suspended substances, conversion of insoluble salts into soluble ones) is sent to a demineralization unit with 7-step evaporation in vertical film-type vessels. Demineralized water with total salt content up to 50 mg/1 is used for feeding boilers at a central heating-and-power plant and for process requirements. Concentrated salt solutions with salt content up to 50 g/1, formed during demineralization, are pumped into deep layers of earth's crust. Pumping is carried out to the depth of 1650-1750 m where stratal water was found with the same salt composition but with a higher concentration – up to 150 g/1.

Organic-polluted water and sewage (of the production plant and municipal) are sent to biological treatment plant where they undergo separate mechanical treatment and then joint biological treatment; after that they are sent to a buffer pond.

Waste water with mineral content up to 3 g/1 and storm (rain) water are sent to the same buffer pond without preliminary treatment.

The complex route includes after-treatment of biologically treated and low-mineral waste water at adsorption and ion-exchange units with the production of nitrogen fertilizers from solutions used for regeneration of ion-exchange resins.

Treated waste water from the buffer pond with salt content up to 1500 mg/1 and chemical oxygen demand ХПК – 30-130 mg/1 is delivered to an adsorption unit for the separation of chloroorganic and other pollutants. An adsorbent is an activated anthracite with 0,25-1 mm particle size. Activated carbon is suspended in the adsorber with constant relative expansion of adsorbent bed being $\frac{N}{N_c} = 1{,}5$.

Spent activated anthracite is discharged from the lower part of the adsorber and sent to a vacuum filter for water separation and then it is delivered to a reactor of adsorbent thermal regeneration. Regeneration is carried out at 850-950°C by a mixture of stack gases and steam. Activated anthracite losses during the cycle (up to 10 per cent of adsorbent being regenerated) are compensated using an anthracite activation unit.

Water after adsorption treatment goes to quartz press filters for separation of entrained carbon dust (particles up to 0,25 mm) and then to rapid filters. Waste water treatment in prefilters and rapid filters is improved by means of polyacrylamide introduction (up to 2 g/m^3).

Filtering rate in press filters and rapid filters is the same – 8 m^3/m^2hr. The filters are periodically washed with a reverse water current. Washing water is separated from suspended carbon in precipitation tanks and recycled.

Waste water free of organic impurities and carbon dust is delivered to the ion-exchange unit for lowering of salt content.

A high-acid cationite KY-2 is used as cation-exchange resin and a high-base anionite AB-17-8 is used as an anion-exchange resin. At H-cationation cationites Ca^{++}, Mg^{++} and partially Na^{+} are extracted from the waste water. After H-cationation water is separated from carbon dioxide in a degasing vessel by venting off with air. Water being separated of carbon dioxide undergoes OH-anionation and then is used for additional feeding of water circulation systems and for other production requirements.

H-cationite filters are regenerated with 25 per cent nitric acid; spent regeneration solution passes successively through 4 receivers, the capacity of each being about ¼ of the volume of all the regeneration solution. Solution from the second receiver, the most saturated with salts, is delivered to a mixer-neutralizer. Solutions from the other receivers are successively used for further regeneration.

OH–anionite filters are regenerated with 10 per cent ammonia liquor. The most concentrated solution after OH–filters regeneration passes to the mixer-neutralizer where the mixture pH is raised to 7 adding, if necessary, 25 per cent nitric acid or 10 per cent ammonia liquor.

As a result of reaction between $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ sludge $CaSO_4\ 2H_2O$ is formed in the neutralizer; it is accumulated in the precipitation tank, centrifugated for separation of solution and sent to heap.

The neutralized solution and centrifugate are collected in tanks from which they are continuosly sent to the production of mineral fertilizers. The fertilizers contain nitrates of ammonium, calcium, magnesium, sodium, calcium sulfate and other compounds. Total fertilizer nitrogen content is about 30 per cent.

Local plants are rather complicate treatment facilities providing for waste water treatment, after-treatment, use and utilization of sludge and other wastes, etc. Thus waste water formed in acetylene production contains carbon black, resin, phenol and other substances. The treatment is carried out in horizontal vessels where carbon black comes to the surface and by means of a rake conveyor is delivered to a mixer and then to a waste combustion unit. Water passed through carbon black separators contains residual carbon black as wwell as resins, phenols, aromatic compounds and other products of incomplete combustion and methane pyrolysis. Because of the lack of treatment methods such waste water is repeatedly used in a separate waste water circulation system. Owing to water evaporation in the water circulation system because of cooling salt content, hardness, alkalinity, etc. rise and this has an adverse effect on the production process. To stabilize recycled water composition it is necessary to continuously purge the circulation system. However because of a high concentration of pollutants in the recycled water it is not allowed to send it to biological treatment or dispose it directly to a water reservoir. That is why the following after-treatment was suggested:

a) coagulation in a suspended bed in clarifier using coagulants of aluminium sulphate, ferric sulphate and chloride. To keep the necessary pH value 5 per cent lime milk is fed to the clarifier. Waste water treatment is effected by means of coagulation on flake surface and adsorption by flake is effected by means of filtering large carbon black particles and small coagulant flakes through the suspended bed.

Sludge formed during treatment (its volume is 0,2-0,5 per cent of the volume of water being treated) contains carbon black, phenols, resins, etc; it is separated from water in drum vacuum filters and sent to heap.

b) waste water treated in a suspended bed is delivered to a contact vessel for treatment with ozone that bubbles through the water layer. Ozone concentration is 20-30 mg/l.

Bubbling is effected through the system of porous porolit pipes that allows to use all the ozone. Ozone-treated water is recycled to acetylene production for cooling of heat exchangers.

Investments in water supply and treatment facilities of a production plant are lowered owing to the reduction of fresh water consumption by 36 per cent and possibility of nitrogen fertilizer production makes operation of treatment facilities profitable because operating expenditure would be justified by the cost of fertilizers.

Development of a complex route allowing to completely eliminate waste water disposal to water reservoirs indicates practical and economic way for solution of one of the most acute problems – that of control of water pollution with industrial effluents and economic use of water resources.

As far as mineral fertilizer plants is concerned there was also developed a water supply route providing for industrial waste water treatment and recycling. These plants are characterized by use of large amounts of water for cooling and as a rule they have large water circulation systems. Water circulation systems are continuously fed with fresh water to compensate losses from evaporation, spray carrying away and water removal to keep constant salt concentration of recycled water.

Large amounts of water are also used in production processes for scrubber refluxing when removing exhaust gases, for washing of pipelines and vessels, for phosphorus washing in storage tanks and precipitators, for dust removal, etc. Main pollutants in waste water here are phosphorus compounds, phenols, cyanides, fluorides, etc.

Experience of operating mineral fertilizer plants shows that it is enough to separate from recycled water only those impurities that may complicate the production process. Thus instead of deep treatment to sanitary limits it is acceptable to carry out treatment to a degree allowing to recycle water to various processes. So phosphorus concentration may be 10 mg/1, that of suspended substances - up to 100 mg/1; fluorine concentration 20-30 mg/1. This is much higher than the sanitary regulations allow and such water should not be disposed to open water reservoirs but it may be recycled.

According to this route treatment plants consist of a neutralization unit with the necessary reagent equipment and facilities for various mechanical and physico-chemical treatment of waste water.

Industrial effluents giving as a rule acid reaction (pH = 1-5) are delivered to a horizontal sand trap for the precipitation of large-size mechanical impurities. Then the effluents are sent to a tank for averaging of waste water amount and composition and levelling out of peak concentrations of impurities including acids. Averaging is carried out for 8 hours. The averaging tank consists of two sections with corrosion-proof coating. There are perforated vinyl pipes on the bottom of the tank for compressed air delivery (air pressure being 10 m of water gaugs). The air contributes to better averaging and acid gas venting off. Air flow rate is 2 m^3 per 1 m^2 of the averaging tanks surface area. Waste water with the averaged composition comes to a mixer where 10 per cent lime milk is continuously added. There is an automatic pH-meter at the mixer outlet for the control of lime milk supply. Waste water from the mixer goes to the precipitator where 0,5 per cent polyacrylamide is added to improve precipitation efficiency and accelerate phase separation. 20-50 g of polyacrylamide are added per 1 tonne of dry matter of waste water suspended substances. Polyacrylamide addition is controlled automatically depending on the amount of waste water to be treated. Neutralization reaction is completed in a reaction chamber presenting a round concrete tank with a capacity - 200 m^3. Normal waste water residence time in the reaction chamber is 30 min. Waste water mixing is carried out by compressed air delivered by means of perforated vinyl pipes. After the reaction chamber waste water is sent to 1250 m^3 horizontal precipitators for the precipitation of suspended substances. Normal waste water residence time in precipitators - 4 hours. The neutralized waste water being clarified, sludge is collected in the lower conical part of the precipitators (sludge humidity is 85-95 per cent). Clarified waste water is recycled to the production process.

Sludge undergoes mechanical water removal in drum vacuum filters. Filtering area of each vacuum filter - 10 m^2, vacuum is kept to be 350-420 mm Hg, filter deposit height - 6-8 mm. Dewa

Irretrievable water losses with sludge, during slag granulation, etc. prevent accumulation of undesirable impurities in a closed water circulation systems. Experience gained at mineral fertilizer plants indicated possibility of water circulation system with a negative balance, i.e. under such conditions when a closed system should be continuosly fed with water from outer water supply sources. As a such a source it is suggested to use water removed from circulation system to keep constant salt composition of recycled cooling water.

Today some mineral fertilizer plants are being converted to water supply routes without waste water disposal.

Practically at each chemical plant there may be used one of the above-described water supply routes characterized by absence of waste water disposal to open water reservoirs and minimum consumption of fresh water mainly for additional feeding of water circulation systems and for covering central heating-and-power plant requirements. According to the next five-year plan for 1976-1980 wide use of such routes is planned at chemical plants.

THE ROLE OF ACTIVATED CARBON IN PHYSICO-CHEMICAL TREATMENT(*)

Walter J. Weber, Jr.(**)

INTRODUCTION

Activated carbon is utilized in a number of environmental process applications. Purification of gases with activated carbon is an effective technique for air pollution control, adsorption of dissolved impurities on carbon is widely employed for water purification, and adsorption on carbon is an integral part of most physicochemical process schemes for wastewater treatment and water reclamation.

The reasons for the choice of activated carbon as an adsorbent in these applications are several fold. Carbon has been demonstrated to have good sorption characteristics for most organic compounds of interest in these fields. This is attributable to its dual properties of large surface area per unit weight (and bulk volume) and high degree of surface activity. It can be produced with relative ease and at reasonable cost from a number of different raw materials and with a variety of surface properties to meet the requirements of specific applications. Finally, activated carbon – particularly granular activated carbon – can be efficiently regenerated for multiple reuse as an adsorbent. Despite exhaustive searches for alternatives, no other material has been found which combines the desirable properties of an adsorbent as effectively as does activated carbon.

This paper discusses salient features of the role of activated carbon in physicochemical treatment systems for municipal and industrial wastewaters, highlighting advantages over other purification processes, and defining factors and considerations involved in the use of carbon adsorption systems.

PRINCIPLES OF ADSORPTION

Adsorption occurs in large measure as a resultant of forces active within phase boundaries, or surface boundaries. These forces result in characteristic boundary energies. Classical chemistry defines the properties of a system by the properties of its mass; for surface phenomena the significant properties are those of the surface or boundary.

Pure liquids tend to reduce their free surface energy through the action of surface tension. A large number of soluble materials (e.g., detergents) can effectively alter the surfaces tension of a liquid. A material which is active at surfaces will decrease the tension at the surface of a liquid by virtue of its movement to the surface. Migration to the surface or boundary results in a net reduction of the work required to enlarge the surface area, the reduction being proportional to the concentration of sorbate at the surface. Hence the energy balance of the system favors the adsorptive concentration of such surface-active substances at the phase interface. The tendency of an impurity to lower the surface tension of water is referred to as hydrophobicity; that is, the impurity "dislikes" water.

Adsorption of a dissolved impurity from water onto activated carbon may result from the hydrophobicity of the impurity, or it may be caused by a high affinity of the solute for the carbon. For the majority of systems encountered in water and waste treatment, adsorption results from a combination of these factors.

The solubility of a substance in water is significant; solubility can be thought of as the chemical compatibility between the water and the solute. The more hydrophilic the substance the less likely it is to be adsorbed. Conversely, a hydrophobic substance will more likely be adsorbed.

In the context of solute affinity for the solid, it is common to distinguish between three types of adsorption. The affinity may be predominantly due to: 1) electrical attraction of the solute to the sorbent (exchange adsorption); 2) van der Waals attraction (physical or ideal adsorption); or, 3) chemical reaction (chemisorption or chemical adsorption).

Many adsorptions of organic substances by activated carbon result from specific interactions between functional groups on the sorbate and on the surface of the sorbent. These interactions may be designated as "specific adsorptions." It is possible for specific adsorptions to exhibit a large range of binding energies, from values commonly associated with "physical" adsorption to higher energies involved in "chemisorption." The adsorptive interactions of aromatic hydroxyl and nitro-substitutes compounds with active carbon, for example, are specific adsorption processes resulting from the formation of donor-acceptor complexes of the organic molecule with surface carbonyl oxygen groups, with adsorption continuing after these sites are exhausted via complexation with the rings of the basal planes of the carbon microcrystallite.[1]

Adsorption results in the removal of solutes from solution and their concentration at a surface, to such time as the amount of solute remaining in solution is in equilibrium with that at the surface. This equilibrium is described by expressing the amount of solute adsorbed per unit weight of sorbent q_e, as a function of C, the concentration of solute remaining in solution. An expression of this type is termed an adsorption isotherm.

The adsorption isotherm is useful for representing the

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capacity of an activated carbon for adsorbing organics from a waste, and in providing description of the functional dependence of capacity on the concentration of pollutant. The steeper the isotherm, the more effective is the activated carbon; that is, the sharper the rise of the isotherm to a given ultimate capacity as concentration increases, the higher will be the effective capacity at the concentration level desired for the treated water. Experimental determination of the isotherm is routine practice in evaluating the feasibility of adsorption for treatment, in selecting a carbon, and in estimating carbon dosage requirements. Mathematic description of the adsorption isotherm for a particular system – that is, the functional dependence of capacity of concentration – is also required for development of predictive models for design applications.[1,2] Details of the conventional Langmuir and Freundlich isotherm expressions are readily available in the literature.(1) Mathews and Weber have recently described the use of a more general and widely applicable three-parameter isotherm model.[3]

The adsorption isotherm relates to an equilibrium condition, however, and practical detention times used in most treatment applications do not provide sufficient time for true equilibrium to obtain. Rates of adsorption are thus significant, for the more rapid the approach to equilibrium, the greater is the fraction of equilibrium capacity utilized in a given contact time. There are essentially three consecutive steps in the adsorption of materials from solution by porous sorbents such as activated carbon. The first of these is the transport of the adsorbate through a surface film to the exterior of the adsorbent ("film diffusion").

Film, penetration, boundary layer, and other theories have been postulated to explain mass transfer in the region separating a turbulent bulk solution and a solid surface. However, the fluid mechanics of this region are not well defined. Boundary layer theory accounts for a velocity distribution and is more realistic than film theory, which assumes a laminar film surrounding the particle. The term "film diffusion" is used here to generally describe the resistance to mass transfer at the surface of the particle. However, use of this term is not intended to imply the existence of a definable film nor is it meant to restrict treatment of data to the film theory. The second of the three consecutive steps in sorption by porous sorbents, with the exception of a small amount of adsorption that occurs on the exterior surface of the sorbent after transport across the exterior film, is the diffusion of the sorbate within the pores of the sorbent and/or along pore-wall surfaces ("intraparticle diffusion"). The third and final step is adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the sorbent.

Consideration of rates at which interfacial tensions are lowered by chemical compounds representative of organic pollution materials gives indication that the adsorption process itself is probably not rate-determining, and that a much slower process must control the overall rate of uptake by porous carbon. Under certain operating conditions, transport of the sorbate through the "surface film" or boundary layer to the sorbent may be rate-limiting; if sufficient turbulence is provided, transport of the sorbate within the porous carbon may control the rate of uptake. One of the most significant factors to consider is, therefore, the nature of the step which controls the speed at which the reaction proceeds, in order that the process may be described in terms of appropriate rate expressions and rate parameters.

Certain properties of the sorbate are useful in determining the nature of the rate-controlling step. For example, if intraparticle transport determines the rate of reaction, the size and structure of an individual solute ion or molecule will affect this rate to the extent that it affects molecular mobility.

The rate-controlling step can also be characterized in part by the observed activation energy for the process. A study of the effect of temperature on rate, in addition to yielding information relative to optimum conditions of operation, permits evaluation of the activation energy and is, consequently, a further means for determining the nature of rate-limiting reactions.

For a process in which the overall rate is controlled by a strictly adsorptive reaction the variation of rate should be directly proportional to the concentration of solute, and for very simple diffusion the rate is expected also to be proportional to the first power of concentration. However, complex mathematic expressions for intraparticle transport indicate that the relationship between concentration and the rate of the reaction will not be one of direct proportionality.[2,3] Since concentration affects a number of the parameters of these equations, it is not possible to predict an exact concentration-rate relation for this reaction. Qualitatively, if diffusion of solute within the pores and capillaries of the carbon limits the rate, the variation of rate with concentration is not expected to be linear, whereas a direct proportionality is anticipated for strictly adsorptive reactions. Thus the concentration-dependence of the rate of reaction may be used as a partial test of hypotheses regarding the nature of the rate-controlling step. The effect of the concentration of solute on the speed at which its sorptive uptake proceeds is also significant for any prediction of the most efficient manner in which adsorption can be utilized for removal of the solute from solution.

For processes in which the rate-limiting reaction is adsorption on the exterior surfaces of the sorbent or transport through an external surface film, the rate is expected to vary as the reciprocal of the diameter of the sorbent particles for a given total weight of sorbent; this because the rate is in this case a first-order function of exterior surface area, which in turn is inversely proportional to particle diameter. Conversely, according to appropriate mathematical expressions for transport relationships, the rate of diffusion of solute into the pores of a particle will vary as the reciprocal of some higher power of the diameter of the particle. Variation of rate with particle size is then another method which is useful for the characterization of the rate-limiting step for a particular system. Particle size is an important consideration also for achieving optimum utilization of a sorbent in treatment operations.

COMPONENTS AND CONDITIONS

Properties of Activated Carbon

Activated carbon is a generic term for a broad range of amorphous carbon-based materials so prepared as to exhibit a high degree of porosity and an extensive associated surface area. Hundreds of different commercial activated carbons with unique properties, and therefore different application suitability, exist.

The purification properties of carbons, or at least charcoal, have been known for over 30 centuries, but the first commercial application appears to have been the use of bone char for decolorization in the cane sugar industry in the 1780's, and bone char is yet the most commonly used sorbent in the cane sugar industry today.(4)

During the 19th century different relatively crude activated carbons were prepared from a variety of raw materials, but manufacturing problems, and the absence of a real need to find anything significantly better than bone char stifled product development. The first activated carbon preparation and use for purification of potable water occurred in 1862.(5)

In the late 1890's and early 1900's Ostrejko developed two improved processes for the manufacture of activated carbon.(6) The first involved the carbonization of vegetable substances impregnated with metallic chlorides; the second the activation of charcoal with carbon dioxide and steam at high temperatures. Virtually all activated carbons are yet made by one or the other of these two processes, either low temperature chemical activation or high temperature gaseous oxidation. The low temperature chemical activation involves chemical dehydration and charring of a carbonaceous raw material, and usually is carried out at temperatures between 200 and 650°C.

Porosity is developed by the action of dehydrating chemicals–normally phosphoric acid, zinc chloride and/or sulfuric acid–on the cellulose structure of the starting material, or by the action of oxidizing gases generated in the process. In the high temperature oxidation of a previously charred carbonaceous substance, a porous structure is developed in the low surface area carbonaceous starting material by controlled oxidation at temperatures between 800 and 950°C with steam, flue gas, or some other oxidizing gas mixture. Bone charcoal is manufactured by a different process, in which collagen and other carbon containing components of bone are carbonized at high temperatures in the absence of oxidizing gases to form carbon deposits within the hydroxyapatite structure of bone.

The properties of an activated carbon depend on the nature of the raw material used, the conditions under which carbonization is accomplished, the activation process and conditions, and post treatment of the product.

Surface areas usually range between 450 and 1500 m^2/g. Bone charcoal is an exception, having, in the freshly prepared form, an area of about 100 m^2/g char. Bone char, however, contains only 5 to 12% by weight of carbon, which accounts for 50% of its surface. The carbon present is truly in an activated state, having an area of between 400 and 1000 m^2/g carbon, depending on the composition of the char.

The surface areas of some typical carbons are shown in Table 1.[7]

TABLE 1.
SURFACE AREAS OF TYPICAL ACTIVATED CARBONS

Name	Origin	Area, m^2/g
Actibon S	Wood	850 – 900
Columbia G	Coconut shell	1100 – 1150
Columbia AC	Coconut shell	1200 – 1400
Darco S51	Lignite	500 – 550
Darco G60	Lignite	750 – 800
Darco KB	Wood	950 – 1000
Filtrasorb 100 & 200	Coal	850 – 900
Filtrasorb 300	Coal	950 – 1050
Filtrasorb 400	Coal	1050 – 1200
Norit	Wood	600 – 800
Nuchar Aqua	Pupl mill residue	550 – 650
Nuchar WV–W	Coal	800 – 900
Nuchar WV–G	Coal	1000 – 1100
Witco 718	Petroleum residue	1100 – 1200

Surface area is normally determined by measuring the volume of nitrogen gas adsorbed at liquid nitrogen temperature (-195°C) at various pressures. From this data one can calculate, using the BET equation, the monolayer coverage and the surface area.[1] The actual area available for adsorption of a specific compound from water can be considerably less than the total surface area determined by nitrogen adsorption.

For gas adsorbing carbons, for example, most of the surface area is in micropores, and these carbons have little capacity for molecules too large to enter a pore less than about 200 A in diameter. As another example, bone char has a surface area of about 65 m^2/g. Typical commercial granular activated carbons may have areas in excess of 100 m^2/g; these, however, have only between 5 and 10 times the capacity of bone char in a use such as sugar decolorization. Based on total surface area alone they should be over 15 times as active, but bone char has a much lower proportion of its surface in micropores and thus more readily available for sorption of the large color bodies. The conclusion that must be reached then is that total surface area is not by itself a satisfactory measure of available surface for liquid phase applications. Rather, it is the distribution of surface area as a function of pore size within the sorbent which is important.

Pore volume distribution can be determined by a combination of mercury porosimetry and gas adsorption-desorption measurements. Gas carbons are characterized by a large percentage of pore volume in micropores, the almost total absence of pore volume in transitional pores, and a secondary maximum in macropores. Conversely, liquid phase carbons have a pronounced percentage of pore volume in transitional pores together with capacity in both micro and macropores. Thus, just as with total surface area, total pore volume is not acceptable by itself as a measure of capacity. Total pore volumes of gas and liquid phase carbons are similar, but it is the pore volume in large pores which determines in large measure the capacity of liquid phase carbons. Together, total surface area and total pore volume thus given some measure of the potential capacity of a carbon, which depends on the distribution of area or volume with pore size, and the distribution of molecular sizes to be adsorbed.

The chemical properties of the surface of the activated carbon are also important in determining activity; that is, capacity for a specific adsorbate. The chemical properties of the surface depend on the starting material, the activation process, and the conditions employed in activation.

Activated carbon can be considered to consist of essentially two types of surfaces, excluding contributions from inorganic impurities. The first are planar, non-polar surfaces, which comprise the bulk of the surface for most carbons. Adsorption on this surface would be largely of the van der Waals type. The second type of surface is comprised of the heterogeneous edges of the carbon planes, which made up the crystallites, whereon carbon-oxygen functional groups formed by oxidation in the manufacturing process are located. These groups, which include phenolic hydroxyl, alcoholic hydroxyl, carboxyl, n-lactone, f-lactone and chromene groups, enable activated carbon surfaces to undergo halogenation, hydrogenation, oxidation, and to act as a catalyst in many reactions.

The surface properties of different carbons can have profound effects on both rate and capacity for adsorption. The surface chemistry of active carbon has been a subject of much interest for some time, yet surprisingly little is known about the nature of the surface functional groups of this material. Recent work in our laboratories has provided an examination of the character of functional groups formed on active carbon under different conditions of activation, using the technique of multiple internal reflectance spectroscopy (MIRS) as a means for characterizing surface functional groups.[1]

While the activity of a sorbent is related to its distribution of surface area and the chemistry of that surface, it must be recognized that activity or capacity is only one parameter which must be taken into account when selecting a carbon for a particular process. Other properties to be considered include hardness and head-loss characteristics for granular carbons, filterability and bulk density for powdered carbons, water solubility of impurities, and pH.

As already noted it is not possible to determine activity or capacity from basic carbon properties such as surface area, not to relate activity for a water or effluent application to capacity for a reference sorbate, such as iodine or methylene blue. Activity or capacity must be determined directly on the system of interest. For granular carbons, hardness is probably second in importance to capacity among properties to be considered in carbon selection. Hardness determines, in large measure, the loss on each adsorption-regeneration cycle. Losses result from attrition on handling and burn-off during reactivation. For coalbased carbons, losses of about 5% per cycle can be expected; losses for softer carbons can be as high as 15% or more.

Head-loss or pressure drop in downflow columns and bed expansion in upflow columns of granular carbon are determined in part by particle size and size distribution; these properties are therefore factors influencing design installation and capital costs. In general, the smallest size of particle that conditions of efficient operation permit should be used, for this increases the adsorption rate and thus reduces the size of the plant required. For powdered carbon, which usually must be removed from the treated water by filtration, filterability is affected by particle shape, size and size distribution.

Bulk density is also important in the selection of a powdered carbon, for it determines, to a large extent, the length of the filtration cycle. Filterability is important, for poor filtration results in the use of more carbon and filter aid, and the need to provide a larger plant.

All carbons contain some soluble impurities depending on the nature of the starting material, the activation process, and final treatment. The amounts and the nature of the compounds which can be tolerated will be governed by the purity requirements of the treated water or effluent.

The "pH" of a carbon is actually the pH measured on a water extract from the carbon. It is a function primarily of the nature of the activation process; steam activation usually yields alkaline carbons, while activation with phosphoric acid, for example, gives carbon pH values below 5. The pH of carbon can be modified by washing. Steam activated carbons can be acid washed to give products with pH values between 5 and 7, while phosphoric acid carbons can be "neutralized" by caustic wash. The adsorption of many solutes can be related to solubility, which in turn is affected by pH. The optimum pH of the carbon, as well as of the solution, can be determined only by experiment with the specific waste water to be treated.

Solute Properties

In general, an inverse relationship between the extent of adsorption of a solute and its water solubility can be anticipated. The water solubility of organic compounds within a particular chemical class decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater. Thus, adsorption from aqueous solution increases as an homologous series is ascended, largely because the expulsion of increasingly large hydrophobic molecules from water permits an increasing number of water-water bonds to reform.

Molecular size is of significance if the adsorption rate is controlled by intraparticle transport, in which case the reaction generally proceeds more rapidly the smaller the adsorbate molecule. It must be emphasized, however, that the rate depends on class or series of molecules. Large molecules of one chemical class may sorb more rapidly than smaller ones of another if higher energies (driving forces) are involved.[1]

Many organic compounds exist, or have the potential of existing, as ionic species. Fatty acids, phenolic species, amines, and many pesticides are a few materials having the property of ionizing under appropriate conditions of pH. Activated carbon commonly carries a net negative surface charge; further, many of the physical and chemical properties of certain compounds undergo changes upon ionization. Most observations point to the generalization that as long as compounds are structurally simple, sorption is at a minimum for charged species and at a maximum for neutral species. As compounds become more complex, the effect of ionization decreases. Studies of amphoteric compounds indicate an adsorption maximum at the isoelectric point, consistent with other observations that adsorption is at a maximum for neutral species. A polar solute will be strongly sorbed from a non-polar solvent by a polar sorbent, but will prefer a polar solvent to a non-polar sorbent. Polarity of organic compounds is a function of charge separation within the molecule. Almost any asymmetric compound will be more or less polar, but several types of functional groups tend to produce fairly high polarities in compounds. Examples of these are hydroxyl, carboxyl, nitro, nitrile, carbonyl, sulfonate, and amine. Thus ethanol, C_2H_5OH, is polar, having an incremental negative charge on the hydroxyl and a corresponding positive charge on the ethyl group. Because solvation by water involves formation of a hydrogen bond from one of the positively charged hydrogens of the water to a group bearing more or less of a negative charge along with some bonding in the reverse direction to the water oxygen, water solubility is expected to increase with increasing polarity. It therefore follows that adsorption decreases as polarity increases, even though active carbon is a polar sorbent.

Because hydrogen and hydroxide ions are sorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Further, to the extent to which ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization. In general, adsorption of typical organic pollutants from water is increased with decreasing pH.

Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature. The changes in enthalpy for adsorption are usually of the order of those for condensation or crystallization reactions, thus small variations in temperature tend not to alter the adsorption process in water and effluent treatment to a significant extent.

The organic components of a waste mixture may mutually enhance adsorption, may act relatively independently, or may interfere with one another. Mutual inhibition can be expected if the adsorption affinities of the solutes do not differ by several orders of magnitude and there is no specific interaction between solutes enhancing adsorption. Similarly, because the adsorption of one substance will tend to reduce the number of open sites and, hence, the "concentration" of adsorbent available, mutually depressing effects on rates of adsorption may be predicted.

It should be apparent from the foregoing discussion of the effects of solute character on adsorption that an analytical characterization of the impurities present is helpful to a thoughtful prediction of the effectiveness of activated carbon in wastewater purification.

ADSORBER SYSTEMS

The type of reactor system in which to contact carbon most effectively with the wastewater to be treated is of particular significance for large-scale treatment operations. Rates of adsorption on granular carbon have been found to depend, in significant measure, upon the particle size of the carbon.[1] It is desirable to employ carbon of as small a diameter as conditions of efficient operation permit, so that high rates of sorption obtain. The term "efficient operation" is a key here, for the size of particle chosen will dictate to some extent the type of reactor system in which contact of the carbon with the wastewater will be accomplished. For example, powdered carbon must be used in either a batch or stirred-tank flow reactor; head loss through a bed or column reactor would be prohibitive in most cases. The type of reactor, on the other hand, will dictate to some extent the efficiency of contact, and therefore the efficiency of the sorption reaction.

In batch-type contact processes, a quantity of carbon is mixed continuously with a specific volume of waste until the contaminants have been decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. If powdered carbon is used in this type of system, separation of the spent sorbent from the water may present difficulties. Conversely, the use of large particles, which may be removed more readily when exhausted, requires longer periods of contact, necessitating larger reactors.

Continuous-flow operations have an advantage over batch-type operations because rates of adsorption depend upon the concentration of solute in the solution being treated. Further, plug-flow (PF) or column, reactors have this same type of advantage over completely-mixed-flow (CMF) reactors.[1] For column operation, the carbon is continuously in contact with fresh solution. Consequently, the concentration in the solution in contact with a given layer of carbon in a column changes very slowly. For batch treatment, the concentration of solute in contact with a specific quantity of carbon decreases much more rapidly as sorption proceeds, thereby decreasing the effectiveness of the carbon for removing the solute. These considerations regarding reactor efficiencies, coupled with the difficulty associated with regeneration of powdered carbon, make granular carbon the choice for most municipal and industrial wastewater treatment operations.

Common adsorber systems are illustrated in Figure 1. For any system, a particular combination of flow rate and bed depth is used to give an effective design "contact time," the time required to reduce the organic contaminants from the influent level to the desired effluent level. Flow rates under 10 gpm/ft^2 (407 l/min/m^2) are usually employed to minimize pumping costs associated with high head loss.

Municipal wastewater treatment experience has indicated good treatment at contact times between 30 and 60 minutes. Significantly longer contact times are normally required for industrial waste streams, consistent with generally higher organic concentrations. Adsorption theory and practice indicate that treatment efficiency and economics are favored by higher concentration. Thus, at some industrial installations, concentrated waste streams are treated individually at their respective sources to optimize overall treatment system design and economics.

To provide sufficient removal of the organic loads normally associated with wastewater, and to utilize the carbon most effectively, an approach to countercurrent contact is commonly required. This can be achieved with moving bed adsorbers, or approximated with a number of fixed bed adsorbers in series. In the latter case the lead contactor in a series of adsorption columns is removed from service when the carbon it contains is exhausted (or nearly so) and, after being refilled with fresh carbon, is placed at the end of the series. Each contactor is thus advanced one position in the series by piping and valving arrangements which permit shifting of inflow and outflow points of the series accordingly. As the number of stages increases, the piping and valving arrangement becomes more complex and costly. A compromise between the advantage of employing multiple stages to more effectively utilize the carbon and the cost of each additional stage must be achieved.

Upflow, expanded operation of fixed beds of granular carbon permits the use of small particle sizes for faster adsorption rates, without the associated problems of excessive headloss, air-binding, and fouling with

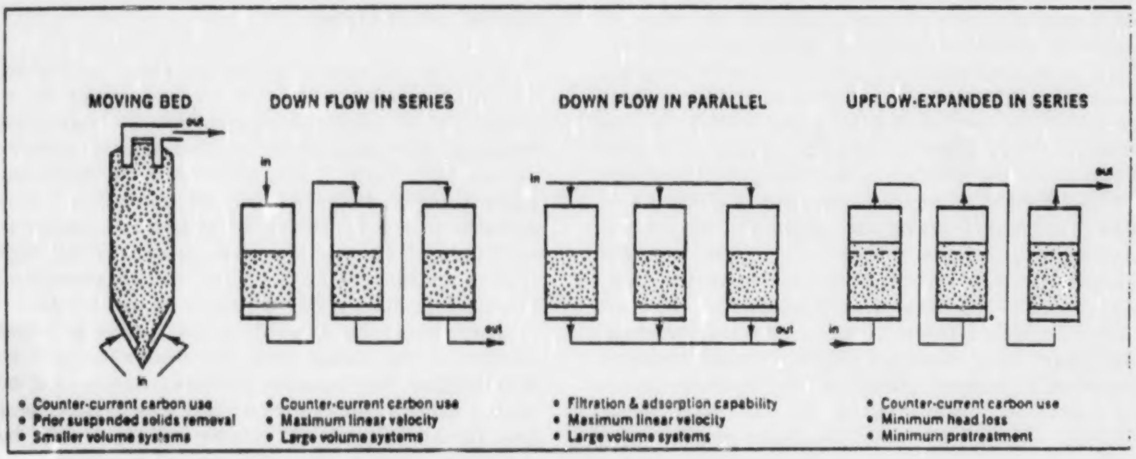

MOVING BED
out
in
• Counter-current carbon use
• Prior suspended solids removal
• Smaller volume systems
DOWN FLOW IN SERIES
in
out
• Counter-current carbon use
• Maximum linear velocity
• Large volume systems
DOWN FLOW IN PARALLEL
in
out
• Filtration & adsorption capability
• Maximum linear velocity
• Large volume systems
UPFLOW-EXPANDED IN SERIES
out
in
• Counter-current carbon use
• Minimum head loss
• Minimum pretreatment

Figure 1. Common Types of Adsorber Systems

particulate matter common to packed-bed operation with fine media. In expanded-bed operation, the water flows upward through a column of relatively fine granular carbon. The advantages of expanded-bed adsorbers over packed-bed adsorbers have been demonstrated and discussed.[8]

For fixed-bed (either packed or expanded) sorption operations, the wastewater to be treated is passed through a stationary bed. Non-steady-state conditions prevail in that the carbon continues to remove increasing amounts of impurities from solution over the entire period of useful operation.

Figure 2 is a plot of the sorption pattern which normally obtains for a fixed-bed non-steady-state sorber. The impurity is sorbed most rapidly and effectively by the first few layers of fresh sorbent during the initial stages of operation. These first layers are in contact with the solution at its highest concentration level, C_0. The small amounts of solute which escape adsorption in the first few layers are then removed from solution in subsequent strata, and essentially no solute escapes from the sorber initially. The primary sorption zone is concentrated near the influent end of the column, the first layers of carbon become practically saturated with solute and less effective for further sorption. Thus, the primary sorption zone moves through the column to regions of fresher sorbent. The wave-like movement of this zone, accompanied by a movement of the C_0 concentration front, occurs at a rate much slower than the linear velocity of the water or effluent. As the primary sorption zone moves through the bed, more and more solute tends to escape in the column effluent, as indicated in the sequence of schematic drawings in Figure 2. The plot of C/C_0 vs time (for a constant flow rate), or volume treated, depicts the increase in the ratio of effluent to influent concentrations as the zone moves through the column. The breakpoint on this curve represents that point in operation where—for all practical purposes—the column is in equilibrium with the influent water, and beyond which little additional removal of solute occurs. At this point, it is desirable to reactivate or replace the carbon.

The method chosen for operation of fixed-bed sorber is dependent on the shape of the curve given by plotting C/C_0 vs time or volume. As noted previously, this curve is referred to as a breakthrough curve. For most sorption operations in water and effluent treatment, breakthrough curves exhibit characteristic non-symmetric "S" shapes, but with varying degrees of steepness and positions of break-point. Factors which affect the actual shape of the curve include the shape of the adsorption isotherm, solute concentration, pH, rate-limiting mechanism for adsorption and nature of the equilibrium conditions, particle size, depth of the column or bed, and the velocity of flow.[1] As a general rule, the time to break-point is decreased by: 1) increased particle size of the sorbent; 2) increased concentration of solute in the influent; 3) increased pH of the water; 4) increased flow rate; and, 5) decreased bed depth. If the total bed depth is smaller than the length of the primary sorption zone required for effective removal of solute from solution, then the concentration of solute in the effluent will rise sharply from the time the effluent is first discharged from the adsorber. Thus, for each type of sorption operation there exists a critical minimum bed depth.

Quantitive prediction of the performance of fixed-bed sorbers involves prediction of the shape and position

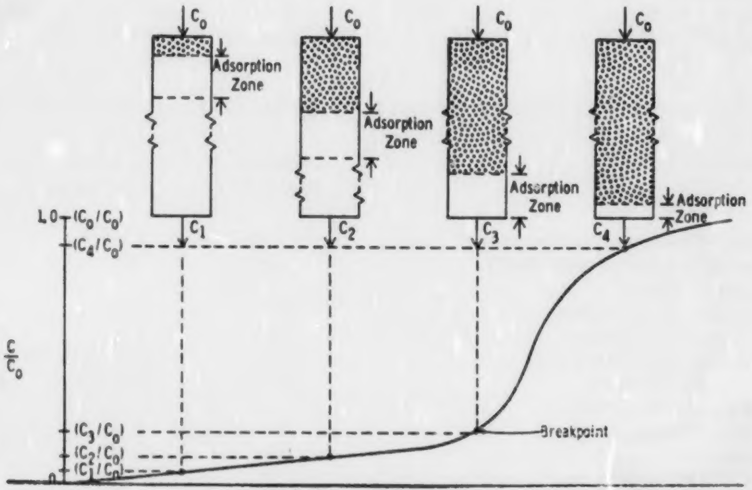


Figure 2. Adsorption Pattern in a Fixed-Bed Adsorber

of the breakthrough curve, representing the movement of the sorption front through an adsorber. Much of the time and expense in planning and designing adsorption facilities is involved in predicting or forecasting the operational dynamics of the adsorption process for a given wastewater stream; this generally requires extensive experimental pilot study. Both the time and expense for such prediction can be minimized by a general modeling scheme which is capable of describing the dynamics of adsorption processes given certain basic information about the system of interest. At a very minimum, a general modeling scheme aids design of programs to be carried out at the pilot level and evaluation of the effects of process and operational variables, thereby easing the transition from pilot to full scale, conserving time and money, and ensuring more optimum full scale design and operation.

Although a detailed discussion of various types of modeling procedures that have been developed for adsorber design is beyond the scope of this paper, it will be noted that Weber and Crittenden have recently developed a general modeling scheme termed MADAM I; Michigan Adsorption Design and Applications Model - I.[2] Based on numeric solution techniques, MADAM I is not restricted to simplified rate and equilibrium expressions to facilitate analytic solution. Rather it can accomodate the dynamic aspects of fluid dispersion, solids mixing, multisolute interactions, and biological growth on activated carbon surfaces, aspects which must be excluded because of mathematic complexity from models which are based on analytic solution techniques.

MUNICIPAL WASTEWATER TREATMENT

A number of physicochemical separation and conversion processes have been studied over the past two decades for potential applications to wastewater treatment. Among these have been adsorption, coagulation, chemical oxidation, solvent extraction, ion exchange, distillation, freezing, reverse osmosis, ultrafiltration, electrodialysis, electrochemical degradation, flotation, and foam separation.(9-11) The process combination of coagulation and precipitation for removal of insoluble impurities followed by sorption on activated carbon for removal of soluble organic impurities has emerged as the treatment sequence of greatest promise in terms of both technologic and economic feasibility.

Development of physicochemical processes for higher levels of treatment centered initially on "tertiary" systems designed to follow "primary" sedimentation and "secondary" biological treatment.(10-11) There are however, several fundamental shortcomings to this approach. First, the implementation of tertiary systems depends upon prior implementation of primary and secondary systems. Second, the addition of tertiary processes to primary and secondary processes incurs capital and operating expenses of such magnitude as to discourage this development in many instances. Third, the effective operation of a tertiary process is dependent to a large extent on the consistent and efficient operation of a biological secondary process, which is normally subject to problems arising from transients in waste composition and flow (often requiring at least partial diversion) and from the occasional presence of toxic materials.

The concept of applying coagulation-sorption processes directly to raw wastes rather than to secondary effluents therefore has derived partially from considerations regarding the effectiveness and reliability of treatment and partially from the relative economics of "direct" versus "tertiary" treatment systems.[12] Direct physicochemical treatment employing coagulation and adsorption subsequently has been demonstrated to be an attractive technical and economic alternative to biological treatment.[13-18]

TABLE 1.
OPERATING RESULTS OF PILOT PHYSICOCHEMICAL TREATMENT PLANTS

Plant	Organic Removal, %	Effluent Concentration
Ewing–Lawrence (New Jersey)	95-98	TOC(i) @ 3–5
Blue Plains (Washington, D.C.)	95-98	TOC = 6
Lebanon (Ohio)		
a. powdered carbonq	95	TOC = 11
b. granular carbon	97	TOC = 6
New Rochelle (New York)	95	COD(ii) = 8
Rocky River (Ohio)	93	BOD(iii) = 8
Salt Lake City (Utah)		
powdered carbon	91	BOD = 13
Owosso (Michigan)	94	BOD = 8

(i) TOC – total organic carbon
(ii) COD – chemical oxygen demand
(iii) BOD – biochemical oxygen demand

With pretreatment of raw waste by chemical clarification—which results in significant removal of both total and soluble organic matter, phosphates and suspended solids—activated carbon treatment commonly produces a clear effluent of low organic content, suitable to meet requirements for pollution control and for many reuse applications.

To give some illustration of this, Table 1 summarizes overall treatment results obtained at several different pilot installations of physicochemical treatment by coagulations and adsorption. More than twenty municipalities in the United States are currently designing, constructing or operating physicochemical facilities for wastewater treatment. The number of industrial treatment facilities using physicochemical processes is an order of magnitude larger; these numbers can be expected to increase sharply within the next decade.

The most common type of adsorber system is one in which the effluent is passed through fixed beds of granular carbon. In such systems hydraulic application rates generally range from 2 gpm/ft^2 to 8 gpm/ft^2 (81-326 l/min/m^2). In this flow range essentially equivalent sorption efficiency is obtained for equivalent contact times. At flow rates below 2 gpm/ft^2 (81 l/min/m^2) sorption efficiency is reduced, while at flow rates above 8 gpm/ft^2 (326 l/min/m^2) excessive pressure drop takes place in packed beds. Contact times employed are in the range of 30 minutes to 60 minutes on an empty bed basis. In general, increases in contact time up to 30 minutes yield proportionate increases in organic removal. Beyond 30 minutes the rate of increase falls off with increases in contact time, and at about 60 minutes the effects of additional contact time become negligible. Carbon beds operated at the lower end of the flow range are generally designed for gravity flow. Systems designed for higher flow rates must employ pressure vessels if packed beds are used. A pressure vessel is more expensive to construct than a gravity flow vessel, but commonly requires less land area, and provides greater ability to handle fluctuations in flow.

Provision must be made to regularly backwash packed-bed carbon systems because they collect suspended solids and tend to develop attached biologic growths in this application. Backwashing alone generally relieves clogging due to suspended solids, but does not completely remove attached biologic growth. It is advisable to include a surface wash and air scour to be assured of removal of gelatinous biologic growth.

This attached growth can lead to development of anaerobic conditions in packed beds. Aeration of the feed is partially effective in preventing anaerobic conditions, but this also accelerates biologic growth to the extent that excessive backwash is required; air-binding can also result. Effective control of biological growth can be accomplished in most instances by regular chlorination of the influent to the adsorbers, and/or by chlorination or caustic addition during regular backwash operations.

Packed beds of granular carbon are well suited for treatment of effluents containing little or no suspended solids, and under such circumstances normally operate effectively for extended periods without clogging or excessive pressure loss. However, the suspended solids invariably present in many wastewaters, and the potential for biologic growth on the surfaces of the carbon can present problems for the use of packed beds. Because solids and biologic activity usually cause progressive clogging and high head loss in packed beds, increased interest has developed in the potential of expanded-bed adsorbers, which have certain inherent operating advantages over packed-bed adsorbers for treating solutions containing suspended solids. By passing wastewater upward through a bed of carbon at velocities sufficient to expand the bed, problems of fouling, plugging and increasing pressure drop are minimized. Effective operation over longer periods of time results, as has been demonstrated in comparative laboratory studies and in field investigations in both "tertiary" and direct physicochemical applications.[8,15,16] Another advantage of the expanded bed, as noted earlier, is the relatively small dependence of pressure drop on particle size. It is possible to use carbon of smaller particle size in an expanded bed than is practical in a packed bed, thus taking advantage of somewhat higher adsorption rates which obtain for smaller particles.

Perhaps the most significant potential benefit provided by expanded-bed adsorption systems for effluent treatment is the apparent extension of the operational capacity of activated carbon observed by Weber *et al*[15,16] who found that apparent sorption capacities in excess of 100 weight-percent as organic matter and 150 weight-percent as chemical oxygen demand (COD) could be obtained in expanded-beds of activated carbon in which biologic growth has allowed to fully develop.[16] Because expanded beds require little maintenance, extended periods of undisturbed operation facilitate the development and continuous growth of bacteria on the carbon surfaces. This biologic growth functions both to biosorb and degrade some organic compounds that would not ordinarily adsorb well on the carbon, and to degrade some of the organic matter which does adsorb on the carbon, functioning to provide *in-situ* partial regeneration by renewing a portion of the carbon surface for continued sorption. Prevention of septic conditions and hydrogen sulfide generation in biologically active adsorbers can be accomplished by addition of small amounts of oxygen or nitrate to the feed to the adsorbers.

Table 2 gives carbon capacities obtained in field operations at several physicochemical pilot plants. In that the wastes, effluent criteria, number of contact states, etc. varied from plant to plant, it is not surprising that some spread in the results is observed. For general planning purposes a COD capacity of 50 weight-percent is reasonable if no biologic extension of carbon capacity is taken into account. This is approximately equivalent to a requirement of 500 pounds of activated carbon per million gallons (60 grams per cubic meter) of sewage treated. However, the results obtained by Weber et al, [16] with biologically-extended adsorption systems suggest that it may be possible to achieve higher effective capacities, reducing the carbon exhaustion rate to less than 200-250 pounds per million gallons (24-30 grams per cubic meter).

TABLE 2.
CARBON CAPACITIES OBTAINED IN PHYSICO-CHEMICAL PILOT PLANTS

Plant	Capacities, weight-percent	
	TOC	COD
Blue Plains (Washington)	15	41
Ewing–Lawrence (New Jersey)*	50	150
New Rochelle (New York)	20-24	60
Lebanon (Ohio)	22	50
Owosso (Michigan)	–	65
Salt Lake City (Utah)	–	36

*Biologically-extended expanded-bed operation[16]

Even for the highest capacities observed, the initial cost of carbon are such as to make regeneration and reuse of this material highly desirable. Technically and economically feasible regeneration of granular activated carbon can be accomplished by controlled heating in a multiple-hearth or rotary-kiln furnace in the presence of steam. During each regeneration cycle some carbon is lost by burning and attrition, and some by alteration of surface properties. The overall loss, expressed as percent by weight of virgin carbon required to restore the total original capacity of the batch, ranges from 5 to 10 percent. For planning purposes, carbon make-up requirements in municipal treatment can be considered to range from 25 to 50 lbs. per million gallons (3-6 grams per cubic meter) of wastewater treated, again not taking account of in-situ biological regeneration.

At present, regeneration systems for powdered carbon are being developed and tested. A successful process for regeneration of the powdered form would represent a significant step toward making treatment system utilizing this lower cost material a technical and economic reality. The key factor will be maintaining carbon loss at a sufficiently low level during regeneration.

A suggested flow sheet for physicochemical treatment of wastewaters is given in Figure 3. In this scheme, coagulant is added to the effluent, and flocculation takes place in a chamber which provides moderate agitation for an average detention time of 15 minutes. Clarification takes place in a sedimentation basin with an average detention time of two hours. The particular flow sheet presented here is a single-stage coagulation system.

The clarified effluent is then passed through activated carbon adsorption units for removal of dissolved organics. The preferred mode of operation is an expanded bed, which permits the use of simple open-top concrete contacting basins and relatively trouble-free operation. The use of open tanks with overflow weirs at the surface of the contacting basin provides a means for additional aeration of the wastewater during treatment, thus helping to control anaerobic conditions in subsequent reactors. Two-stage contacting of the activated carbon is outlined in the treatment sequence given in Figure 3. However, a larger number of stages can be utilized if desired for a particular application. A typical plant layout for a design capacity of 10 million gallons (37,850 cubic meters) per day might be based on five parallel adsorption units of two stages each. When

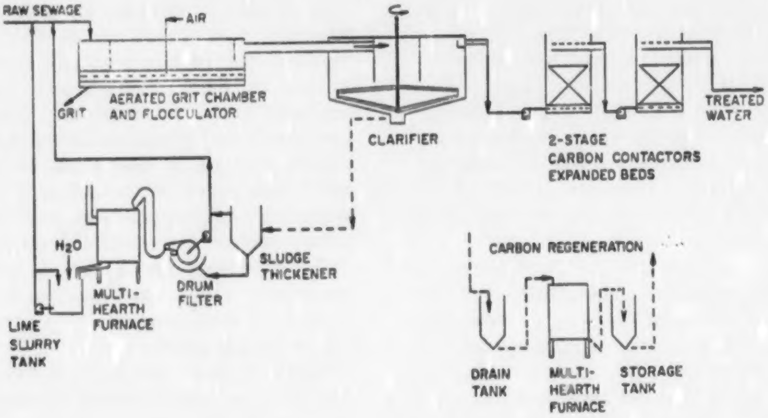


Figure 3. Schematic Diagram of A Typical Physicochemical Treatment System

the granular carbon in the first stage of one unit is spent, that unit can be taken off stream while the spent carbon is removed and regenerated in a furnace provided for this purpose. During the time this unit is off-stream for regeneration, the other four units can run at 25% higher feed rate each. Upon completion of the regeneration, the carbon is returned to the adsorber, which then becomes the second stage of that unit; the former second stage with partially spent carbon becoming the first stage. Feed is then evenly divided to the five units until another carbon bed is spent.

The water resulting from the clarification and activated carbon treatment of municipal wastewaters will enhance the quality of most surface waters, and with disinfection is suitable for many reuse applications. A final filtration may be desirable to insure a crystal clear effluent. This post-filtration would remove any suspended matter passing through, or biologically generated in, the carbon columns.

INDUSTRIAL WASTEWATER TREATMENT

Industrial wastewater treatment is perhaps one of the most effective and widespread environmental application areas for adsorption processes. Experience with a broad range of different types of industrial effluents indicates that treatment by activated carbon is technically and economically suitable for many such applications.

In addition to its use as a sole treatment process, with appropriate pretreatment as required, activated carbon treatment has been applied in some instances to the effluents from biological treatment processes, and in other instances to the influents to biological treatment processes. In the former case adsorption usually is intended for removal of biologically resistant chemicals, such as nitrated aromatics in some chemicals industries. In the latter case, the purpose of adsorption is to remove substances, such as chlorophenol in the pesticide industries, which may be toxic or otherwise capable of inhibiting biological treatment processes.

Pretreatment Requirements

Granular carbon rather than powdered carbon is most commonly utilized for industrial waste treatment; this normally involves the use of either fixed-bed or moving-bed contact systems. Pretreatment in these cases is primarily for removal of excess suspended solids, oils, and greases; materials which, although they can be removed effectively by the adsorption bed, will likely cause problems of head loss, fouling, and plugging of the adsorber.

Suspended solids in amounts exceeding approximately 50 mg/l should be removed prior to adsorption. Oils and greases in concentrations above about 10 mg/l should not be applied directly to adsorption beds. In addition to causing head loss problems, these materials, particularly oils and greases, can coat the carbon particles and reduce adsorption effectiveness dramatically.

For concentrations of suspended solids, oils, and greases below the values given above, carbon beds are frequently used for the dual role of filtration and adsorption. Carbon bed engineering incorporates well established filtration experience regarding backwash requirements, surface wash or air scour features, and appropriate flow rates conducive to filtration. In applying established filtration experience to carbon beds, which are normally deeper than ordinary filters, it has been demonstrated that the top few feet of the carbon bed function in the same manner as the equivalent depth of a conventional single media filter. Backwash bed expansion should be based on this effective filtration depth rather than the total adsorption bed depth.

Chemical clarification, air flotation and filtration are common pretreatment processes. It is not unusual, however, to find that pretreatment is not required when adsorption is applied at the point of origin of the contaminant of concern. Treatment of combined waste streams, on the other hand, invariably requires pretreatment for removal of suspended solids, oil, and grease.

Adjustment of pH is sometimes employed to enhance adsorption efficiency. Dissolved organic compounds are normally adsorbed best at the pH of minimum polarity. For example, weak acids, such as phenol, are better adsorbed at lower pH values, while amines can be expected to adsorb best at higher pH values. Potential advantages of pH adjustment can be quickly determined by laboratory tests.

Flow equalization is desirable for many industrial effluent treatment processes. While adsorber systems can be designed to meet fluctuating influent hydraulic loads and organic concentrations, the treatment system can be more economically designed and operated when these fluctuations are minimized.

Treatability Evaluation

Adsorption isotherm tests are standard first-step procedures for determining the feasibility of adsorption for a specific application. The isotherm indicates the degree of treatment that might be achieved and the approximate amount of carbon required to reach a treatment objective. It also indicates the dependence of the amount of adsorption on contaminant concentration.[1]

The Calgon Corporation has recently tested 222 samples of different industrial effluents, representing 68 different manufacturing operations, to evaluate the removal of organic contaminants by activated carbon.[19]

In the work reported by Calgon, samples were membrane filtered prior to the adsorption tests to remove suspended material which otherwise could be incorrectly associated with adsorption treatment. This is generally a good experimental procedure, and the type and concentration of suspended material removed in this step gives a preliminary indication of the desirability of pretreatment.

The adsorption isotherm results are summarized below, grouped according to SIC classification (Standard Industrial Classification, U.S. Dept. of Commerce) of the wastewater treated. This grouping allows comparison of adsorption performance on like organic contaminants and provides a reference list for indication of the feasibility of adsorption as a treatment for each class of effluent.

The list is a useful reference when considering treatment alternatives available for a specific industrial effluent problem, with respect to a preliminary indication of the feasibility of adsorption treatment. The data presented can be further catagorized according to organic concentration. This categorization is given in Table 4.

Because of the generally high levels of TOC evidenced in most untreated industrial effluents, it is likely that a combination of treatment processes will be required to meet rigorous TOC reduction objectives at lowest cost. The selectivity of adsorption on activated carbon for color and phenol suggests the possibility of using adsorption as a pretreatment to biological systems to remove toxic, inhibitory and bio-resistant substances. Adsorption treatment of industrial effluents for selective removal of specific substances prior to discharge to municipal systems appears to be technically and economically feasible in many instances.

TABLE 3. RESULTS OF ADSORPTION ISOTHERM

SIC number	Type of industry	Number tested	Initial TOC (or phenol), mg/l	Initial color, O.D.	Average % reduction	Carbon exhaustion rate, lb/ 1000 gal
2000	Food and kindered products	16	25–5,300	--	90	0.8–345
2100	Tobacco manufacturers	1	1,030	--	97	58
2200	Textile mill products	33	9–4,670	--	93	1–246
		28	--	0.1–5.4	97	0.1–83
2300	Apparels and allied products	2	390–875	--	75	12–43
2600	Paper and allied products	9	100–3,500	--	90	3.2–156
		1	--	1.4	94	3.7
2700	Printing, publishing and allied industries	2	34–170	--	98	4.3–4.6
2800	Chemicals and allied products	137	19–75,500	--	85	0.7–2,905
		13	(0.1–5,325)	--	99	1.7–185
		18	--	0.7–275	98	1.2–1,328
2900	Petroleum refining and related industries	17	36–4,400	--	92	1.1–141
		3	(7–270)	--	99	6–24

TABLE 4. SUMMARY OF ADSORPTION DATA ON INDUSTRIAL WASTES

Category	Number of samples
Initial TOC < 100 mg/l	24
Initial TOC = 100-1000 mg/l	100
Initial TOC = 1,000-10,000 mg/l	86
Initial TOC > 10,000 mg/l	12
TOC reduction > 90%	140
TOC reduction = 85-90%	29
TOC reduction < 85%	53
Color reduction > 95%	36
Color reduction = 90-95%	5
Color reduction < 90%	1
Phenol reduction > 99%	12
Phenol reduction < 99%	1

TEST ON DIFFERENT INDUSTRIAL WASTES

SIC number	Type of industry	Number tested	Initial TOC (or phenol), mg/l	Initial color, O.D.	Average % reduction	Carbon exhaustion rate, lb/1000 gal.
3000	Rubber and miscellaneous plastic products	8	120–8,375	--	95	5.2–164
3100	Leather and leather products	2	115–9,000	--	95	3–315
3200	Stone, clay and glass products	7	12–8,300	--	87	2.8–300
3300	Primary metal industires	8	11–23,000	--	90	0.5–1,857
3400	Fabricated metal products	1	73,000	--	25	606
3700	Transportation equipment	2	190-2,850	--	91	12-361
4200	Motor freight transportation and warehousing	4	320-3,480	--	87	20-72

Carbon exhaustion rates for industrial effluents are clearly in excess of those associated with municipal effluent treatment. This is expected, considering the relative levels of influent TOC. Municipal effluents can be successfully treated at costs between 15-40 U.S. cents per 1,000 gallons. For the most part, treatment of industrial effluents costs in the dollars per 1,000 gallons category for effective TOC reduction. For selective removal of color or phenol, treatment costs might well be in the cents per 1,000 gallons range.

For certain types of industrial effluents, such as those from textile mill products operations, treatment by adsorption alone appears suitable to meet organic removal objectives. Experience with textile effluents indicates the possibility of water reuse following adsorption treatment. Such reuse can offset pollution abatement costs. Cost reduction opportunities exist for water reuse in many other industrial areas as well. Point source treatment of specific wastes is also a substantial factor in the use of adsorption technology for industrial waste treatment.

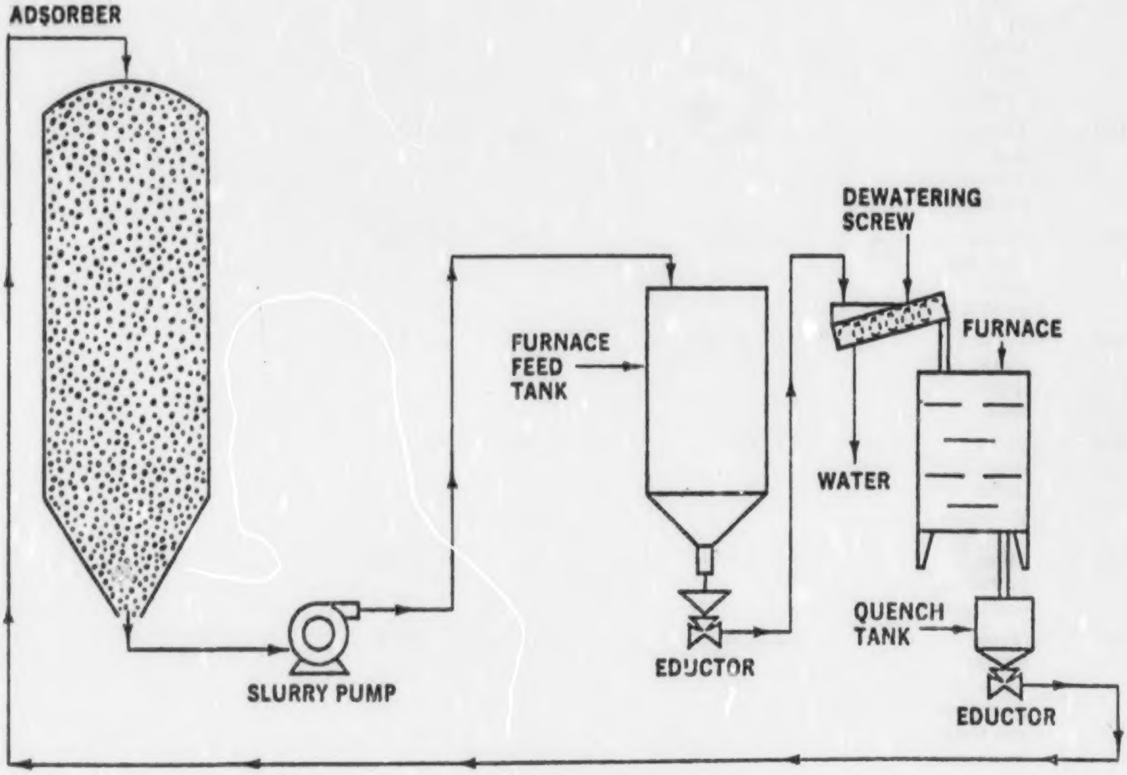
REACTIVATION OF CARBON

Thermal reactivation of granular activated carbon has been a successful practice for several decades. Rotary kilns or multiple-hearth type furnaces operated at temperatures between 1600-1800°F (870-980°C) are normally used. The activation atmosphere in these furnaces is maintained at low oxygen levels to effect selective oxidation of adsorbed organic contaminants rather than of the activated carbon. Carbon losses range between 2-10% per cycle, with larger systems generally experiencing smaller losses. Large systems are normally designed for continuous operation, thereby facilitating control of the process.

Afterburners and scrubbers are used to strip the furnace exhaust gases of air pollutants. Industrial wastes containing halogens or other corrosive substances require special materials of construction in the kiln or furnace to avoid corrosion problems. It is important that each industrial effluent be evaluated from this standpoint.

The process and functional features of a thermal reactivation system are illustrated in Figure 4. Detailed engineering design features of granular activated carbon reactivation systems are readily available in the literature.[20,21]

Experience with chemical reactivation of granular carbon has been largely unsuccessful to date. Recovery of specific by-product adsorbates by extraction has been demonstrated in some instances, but generally the carbon does not sufficiently recover its adsorptive properties. Additionally, by-product recovery frequently suffers from the fact that the material of interest is in a waste mixture and a pure product is difficult to recover.



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THE REMOVAL OF VOLATILE SUSPENDED SOLIDS FROM WASTEWATERS.

I.N. Miasnikov, B.A. Balakin.

The process wastewaters from many industries are contaminated with various volatile suspended solids. A great number of these matters, especially, hydrogen sulphide, carbon sulphide, carbon acid gas, sulphur dioxide are contained in the wastewaters of chemical industries. The wastes of sulphate pulp industries contain hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide. A great number of volatile matters are also contained in the wastes of oil refinery industries and oil fields.

In some cases the volatile suspended solids are formed in the wastewater while its rendering harmless, i.g. in digestion tanks and while using various chemicals at the waste treatment plants. The products of accessory reactions in this case are hydrogen sulphide, methane, carbonic acid gas and etc.

The quantity of volatile suspended solids in the majority of the above mentioned wastes exceeds from 0.5 to 1 g/1. In addition, many of them are toxic even in low concentrations. For instance, the allowable concentration of carbon sulphide in the water of reservoirs is not higher than 1 mg/1, hydrogen sulphide - 0. The necessity of volatile suspended solids removal from wastewaters is due to their toxic influence on biological treatment processes, deterioration of conditions of suspended solids settling, atmosphere contamination and etc. Many of volatile suspended solids are the valuable products and their return to production is also a great national economy significance.

The removal of volatile suspended solids from wastes is very difficult due to the great amount of waste liquid, the availability of many cimponents in the solution to be treated, various concentration of volatile suspended solids and mechanical impurities of unequal commodity value of these components, necessity of high rate treatment. The solution of the problem is also complicated, in most cases, by the absence of data on physical and chemical parameters of wastewater (density, viscosity etc.), the data of solubility of gases and diffusion factors, which are necessary to take into account in practical calculations, associated with the liquid to be treated.

At present in most cases the all-plant wastes contaminated with volatile suspended solids, enter the reservoirs and sewage treatment facilities without preliminary degassing. The operation experience of sewage treatment facilities shows that at the expense of natural degassing through the open surface the satisfactory water treatment from volatile suspended solids is not achieved. For instance, the wastewaters of chemical fibre industries after the treatment facilities contain some volatile components the quantity of which several times exceeds sanitary standards. In addition in the zone of the treatment plant the contamination of atmosphere by the products to be treated is observed.

The efficiency of the natural degassing method through the open water surface of the treatment facilities does not exceed 50-60 per cent. Even when using relatively prolonged settling of wastewaters (up to 15 days) the residual quantity of volatile suspended solids is 3-5 mg/1. Consequently, this method of removing volatile components cannot be recommended neither for sanitary considerations nor for technical and economical indices.

In home and foreign practice various degassing processes are used for the removal of volatile suspended solids from industrial wastes. Water blow-off with air in the open channels and settling tanks is used. Blow-off products often enter the atmosphere.

For degassing separate categories of wastewaters and process solutions the desorbers with the chord nozzle, with the nozzle of Rashig's rings and hollow spraying desorbers are used. The operation experience with nozzle apparatuses and cascade apparatuses shows that the rate of degassing of process solutions at the chemical fibre industries does not exceed 90 per cent. These apparatuses are advisable to use for wastewater treatment.

The degassing of abrasive industries wastewaters from hydrogen sulphide in the apparatus with the nozzle of Rashig's rings provides, as our scientists show, the elimination of dissolved gas by 95 per cent. The nozzle-type and the cascade-type apparatuses are also advisable to use for the removal of hydrogen sulphide, mercaptan, dimethyl sulphide and dimethyl disulphide from the wastewaters of pulp and paper industries.

Most scientists while considering the performance of various desorbers emphasize the efficiency of liquid treatment in the nozzle-type apparatuses. Alongside it is necessary to note that the presense of suspended solids in wastewaters makes the operation of the nozzle-type apparatuses difficult that limitates their application field.

For the degassing of waste liquid the temperature effect is used. The wastewaters are heated when increasing density up to the temperature higher than the boiling point, and then they enter the evaporation chamber though the reducing valve.

In the course of instant boiling the degassing alone takes place. High-temperature vapour and gas mixture formed enters the tubular heat exchanger, where it is cooled at the expense of wastewater flowing to the plant.

The degassing of the liquid in the apparatuses in vacuum is used when it is necessary to perform thorough elimination of dissolved gases when their residual content is I mg/1.

One of the methods of dewatering the volatile suspended solids contained in the liquid, is their transformation into the non-soluble compounds. Chlorination of wastewater is used for rendering harmless hydrogen sulphide and carbon sulphide. Chlorinated lime and chlorine are used as chemicals. The oxidation of carbon sulphide can be performed up to the neutral sulphur or up to SO_3 with subsequent hydration to H_2SO_4. For the oxidation of I g of carbon sulphide into sulphur 0.93 g of available chlorine is required, and for the oxidation into SO_3 - 3.7. The rate of treatment is dependent on the weight ratio of carbon sulphide and chlorine; for example, at the ratio I:2 it exceeds 50 per cent, but at the ratio I:8 it exceeds 90 per cent. The oxidation proceeds in time.

The reaction of hydrogen sulphide with available chlorine proceeds intensively and is completed with the formation of sulphur. At the ratio of hydrogen sulphide and chlorine equal to I:I in the acidic medium 65 per cent of hydrogen sulphide is oxidized in an hour, but in four hours - 80 per cent.

One of the efficient method for rendering harmless hydrogen sulphide, methyl mercaptane and its natrium salts is their air oxidation in ordinary conditions in the presence of catalizers (hydrated oxides and iron oxides, copper oxides, manganese oxides etc.).

At the first stage of oxidation the sulphides of these metals are formed, which then are air oxidized into subsequent compounds of elementary sulphur, thiosulphite and sulphate depending on the ph value.

As a catalizer graphite is also used which allows the total oxidation of hydrogen sulphide-methyl mercaptan, contained in the liquid, as well as the oxidation of their natrium salts to thiosulphate for an hour. When catalizers are absent their air oxidation is performed by 50 per cent during 24 hours.

While considering the given studies and the operation experience of industrial apparatuses it is necessary to note, that the rendering harmless of volatile suspended solids generally does not exceed the sanitary standard.

In addition, the published studies do not contain sufficient data describing the kinetics of treatment process, as well as its structural design. This makes the use of degassing methods in practice difficult and necessitates the usage of subsequent studies with the purpose of determination general process parameters of overall removal of components from the wastewaters at minimum consumption of desorber agent, as well as the specifying of the calculation method for desorbers and determination of technical and economical indices of degassing installations.

With this purpose the institute VNII VODGEO in cooperation with a number of organizations has accomplished the studies as to desorption of dissolved gases in the nozzle-type apparatuses of Rashig's rings with the barbotage layer of liquid, as well as spraying degassing units. The experiment is realized at pilot-scale and full-scale installations, using real wastewaters of various industries.

When calculating the desorption apparatuses it is necessary to take into account a number of physical and chemical parameters of wastewater and the components to be removed. The absense of these data does not allow to carry out the design of degassing works. That's why the attention was given to the determination of quantitative values of density, viscosity of wastewater, equilibrium constants of the components to be removed, as well as to the other physical and chemical indices of liquid and volatile suspended solids.

The equilibrium constant m is dependent on the qualitative characteristic of wastewaters, its value is considerably ranges. The quantitative values of equilibrium constants for carbon sulphide, hydrogen sulphide and carbon acid which are in a free state in the wastewater, containing not more than 3 kilomoles/cu.m. of mattars were determined according to the following formula:

$$m = \frac{m_o}{1 - 2.05(\Sigma C)^{0.76}} \qquad 1$$

where

m_o, m – the equilibrium constant of the component for water and wastewaters.

C – concentration of the matter to mole/cu.m.

The values of equilibrium constants of carbon sulphide and hydrogen sulphide for water and wastewater from the chemical fibre industries, containing from 0.I to 0.2 moles of the electrolite are given in the table.

During the operation of desorbers the degree of water treatment was studied depending on its temperature, pH value, concentration of volatile components and suspended solids, consumption of liquid and desorbing agent, pressure in the apparatus, construction of the water spraying device, geometric parameters of desorbers etc.

The conducted studies allowed to establish the optimum parameters of the wastewater treatment process and to determine the desorbers application field.

Desorption in the nozzle-type apparatus of Rashig's rings.

The removal of volatile suspended solids from wastewaters is performed in the apparatus under vacuum and at the atmospheric pressure. As a nozzle which is located in order or conversely the ceramic Rashig's rings are used with dimensions 25 x 25 x 3 and 50 x 50 x 5. The liquid supply to the desorber is performed through the nozzles with the outlet opening 5 or 10 mm, being located at the height of 0.5 - 0.7 m above the nozzle.

The application of regulable nozzles allows the uniform distribution of liquid to the upper layer of the nozzle.

The desorbing agent is fed under the nozzle through the perforated piping. When using the nozzle the conditions of modelling are taken into account, the ratio of maximum dimension of the element to the desorber diameter is less than 0.125, the nozzle height to the diameter of the apparatus 5, but the ratio of the nozzle height to the diameter of the element 40. On the upper part of the apparatus at the height of 0.3 m above the nozzles the drop removing device of Rashig's rings is placed, the dimensions being 25 x 25 x 3, the height of layer is 0.2 m. The apparatuses are operated at the nozzle spraying density up to 160 cu.m/sq.m/hr.

The amount of the matter being transformed from the liquid into the gaseous phase (and conversely) is determined as to the known mass transfer equation:

$$W_A = K_x . F . \Delta \text{ aver.} \qquad (I)$$

where W_A - quantity of desorbed component,

K_x - mass transter factor related to the unit surface contact of phases;

Δ - average driving force of the process. The driving force of the process was determined according to the formula widely used in practice:

$$\Delta \text{ aver} = \frac{(X_I - X_p \text{ inlet}) - (X_c - X_p \text{ outlet}}{2.3\ 1\ g \quad \dfrac{X_I - X_p \text{ inlet}}{X_2 - X_p \text{ outlet}}}$$

where $X_I X_2$ - the concentration of the component at the outlet and inlet in the apparatus;

$$X_p \text{ inlet} = \frac{V_I}{m}\ ;\ x_p \text{ outlet} = \frac{V_2}{m}$$

equilibrium concentrations;

m – equilibrium constant.

When V_2 is equal to zero and the value X_p inlet is highly low, the driving force is determined according to the formula:

$$\Delta \text{ aver} = \frac{X_I - X_2}{2.3\ \lg \dfrac{X_I}{X_2}} \qquad 3$$

When using the formula (3), the possibility of error as the calculations showed, is 8: + 4 per cent.

The mass transfer factor is the main parameter, which characterizes the operation intensity of the desorption apparatuses. It is dependent on the direction of phases movement, proportional to the spraying density of the nozzle in the range of 10-160 cu.m. sq.m/hr of wastewater. Stable operation of the apparatus is observed when spraying density is not less than 10 cu.m. sq.m./hr. The nozzle resistance does not exceed 20 mm Hg. The optimum unit air consumption for the apparatus operation under vacuum is 3 cu.m/sq.m/hr.

Phase equilibrium ratio values for aqueous solutions of carbon sulphide and hydrogen sulphide.
(Figures in quadratic breaks are obtained by calculation method for temperature above the boiling point of carbon sulphide)

Name of liquid	Pressure in bar. and in mm of merc.col (in brackets)	components	Temperature, °C																	
			0	5	10	15	20	25	30	35	40	45	48.2	49	50	60	70	80	90	100
			constants m																	
Water	1.013	CS_2	350	447	545	734	936	1130	1570	2082	3108	5 826	7 186	[32 790]*	[120 180]	—	—	—	—	—
	(760)	H_2S	270	319	370	428	490	552	611	585	755	835	—	—	896	1040	1210	1370	1450	1490
waste water	1.013	CS_2	598	764	930	1250	1600	1950	2680	3560	5300	9960	12300	[55 510]	[205 100]	—	—	—	—	—
	(760)	H_2S	480	545	630	730	840	940	1060	1170	1290	1430	—	—	1 530	1780	2070	2340	2480	2550
the same	0.733	CS_2	477	610	734	1000	1280	1550	2140	2640	4240	7 950	9 800	[44 730]	[163 800]	—	—	—	—	—
	(560)	H_2S	368	435	505	584	670	753	842	935	1030	1 140	—	—	1220	1420	1650	1870	1980	2030
»	0.613	CS_2	571	725	890	1200	1530	1850	2560	3100	5 010	9 500	11700	[53 600]	[196 000]	—	—	—	—	—
	(360)	H_2S	440	520	604	700	800	900	1000	1120	1230	1 360	—	—	1460	1700	1970	2230	2360	2430
»	0.333	CS_2	1050	1342	1636	2200	2810	3420	4710	6250	9330	17 800	21600	[98 500]	[361 000]	—	—	—	—	—
	(260)	H_2S	811	953	1110	1285	1470	1660	1850	2060	2270	2 510	—	—	2 700	3120	3630	4110	4350	4500
»	0.213	CS_2	1640	2100	2560	[illegible]	4400	5350	7370	9770	14600	27350	33 740	[154 000]	[564 000]	—	—	—	—	—
	(160)	H_2S	1270	1500	1740	2019	2300	2530	2900	3220	3540	3 920	—	—	4200	4800	5680	6430	6800	7000

(0.0I m/sec), at normal pressure - I0 cu.m/sq.m/hr. The increase of air velocity in the desorber up to 0.13 m/sec doesn't practically influence the rate of wastewater treatment.

The main quantity of volatile components (up to 60-80 per cent) is removed from the liquid at the expense of the operation of the spraying devices; the height of their location above the nozzle being 0.7 m. In this case the liquid flows to the nozzle with insignificant amount of gaseous component. As the wastewater flows through the nozzle the volatile products are removed from the liquid.

The value K_x is inversely proportional to pH. The optimum value during the wastewater treatment in the apparatus in vacuum is 6.5. The degree of desorption is 85 per cent. The coefficient of desorption is also dependent on the vacuum value, especially at high spraying densities.

The mass transfer intensity doesn't vary at the increase of the ratio H / more than 3(H - the height of the nozzle, - diameter of the apparatus). The method of nozzle location doesn't greatly influence the treatment effect. The presence of suspended solids in the wastewater which have adhesive properties reduces the time of the operation run of the nozzle. So, for the treatment of wastewaters from the chemical fibre industries not more than 80 mg/l of suspended solids is allowed but for (hard) solids, not having adhesive properties, their content may exceed I g/l and more.

As a result of generalization of the experimental data (when using the theory of similarity and the method of analysis of dimensions) the following criterion equation is obtained for the desorption process in the nozzle-type apparatus:

a) for carbon sulphide $N_4 = A.Re^{0.83}.Pr^{0.5}$ (4)

b) for hydrogen sulphide $N_4 = A.Re^{1.26}.Pr^{0.5}$ (5)

where N_4,Re,Pr - the criteria of Nusselt, Reynolds, Prandtlja. The value of the coefficient A is dependent on the vacuum depth; for carbon sulphide it is in the range of 3.0 (at 200mmHg) to 4.5 (at 600 mm Hg): for hydrogen sulphide - 0.0 and 0.075 respectively.

Values of Reynold's criterion index for carbon sulphide are confirmed by prolonged operation of desorbers when wastewater treatment. The difference of indices is due to the complexity of wastewater composition, to the variety of forms presented in the components to be removed etc.

Thus the given criterion equation allows to determine by the calculation method the mass transfer factor when wastewater treatment. The efficiency of volatile components removal exceeds 98 per cent (the residual content is less than 2 mg/l).

The cost of treatment of I cu.m. wastewater in the nozzle-type apparatus operating in vacuum is 0.7 copeck, but at the atmospheric pressure it is 2 copecks. The latter cost is obtained for the conditions of treatment the foamy liquids in the apparatuses (the influent contains foamy substances) and for air supply by the gas blower. In case of using the fan to feed the desorbing agent the treatment cost of I cu.m. influent is only 0.5 copeck.

When returning valuable components to the process the treatment of influent may become paying.

The desorption in the apparatus with the barbotage layer of liquid.

One of the main components which determine the apparatus design and the method of rendering the volatile contaminants harmless are the suspended solids. In most cases they have adhesive properties; their concentration approaches I g/l and more that, in turn, excludes the possibility of application such efficient desorbers as the nozzle-type apparatuses.

For rendering these wastewaters harmless it is advisable to use degassors with entire barbotage liquid layer. They are efficient for removing from wastewaters weakly soluble gases in which the main resistance during diffusion is represented by the liquid film. At barbotage along with the desorption of volatile contaminations the adsorption of oxygen takes place; as a result, the oxidation processes occur and BOD liquid is reduced in 30-50 per cent and more, that is very significant when wastewater rendering harmless.

To remove the volatile components from the wastewaters which contain some amount of suspended solids it is advisable to use the apparatuses with the barbotage layer of liquid (figure I). The feature of the apparatus is that its design provides for spraying and barbotage of the liquid.

The desorber is in operation both in vacuum and at atmospheric pressure. The air is fed through the removable barbotage device with perforated disc, the dia of openings is equal to I.8 mm. Similar as in the nozzle-type apparatus the liquid is fed through the variety of nozzles with I0 mm outlet opening. The operation of nozzles successfully provides for foam reduction; when they are absent the possibility of the apparatus operation is excluded when the influent containing surface-active agents is treated in it.

The apparatus allows to change (according to the operational conditions) the height of the barbotage layer of liquid by subsequent erection of pipings (9,II,I3). The release, of micro bubbles from the liquid, which are go away from the barbotage layer takes place in the vat (I0); the gas obtained enters the apparatus through the pipings (I3).

The operation of the desorber was studied at the spraying density being 3-66 cu.m/sq.m/hr, and the barbotage intensity I6-360 cu.m/sq.m/hr.

During the operation along with the other parameters static (h st) and working (work) height of liquid layer barbotage is determined and this allowed to establish gas content of the layer - the value Φ , which is the most important characteristics.

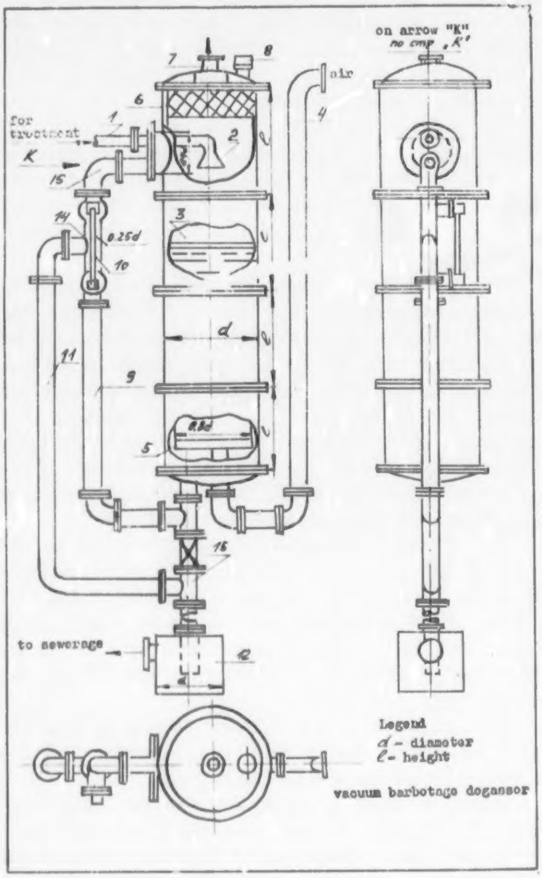
The average diameter of the air bubble for the above mentioned wastewater barbotage conditions may be assumed as 3.8 mm on the basis of calculations. Contact surface of phases when barbotage may be presented as summary surface of gas bubbles of gas liquid system. In this case the unit contact surface of phases related to I cu.m. of the gas liquid layer is determined according to the known formula:

$$\alpha = \frac{6\varphi}{d \cdot \alpha\nu} \qquad 6$$

Contact surface of phases, related to I sq.m. of the desorber cross-section is determined according to the

$$\alpha_s = \frac{6\varphi \cdot h\ bar}{d \cdot \alpha\nu} \qquad 7$$

For the calculation of desorption the main mass transfer equation is applicable (I). The mass transfer factor K_x is proportional to the spraying density. For the operation of degassing units in vacuum the intensity of barbotage 60cu.m/sq.m/hr (unit flow rate 5) is optimum and at normal pressure -I20-I60 cu.m.sq.m/hr (unit flow rate I0-I5).



vacuum barbotage degassor

Рис.1

These parameters I.5-2 times nigher than for the nozzle-type apparatus of Rashig's rings. The studies showed that the mass transfer rate is dependent on the vacuum value, especially, at high flow-rates of the liquid. The experiment showed that the increase of the ratio H/D (liquid layer height, degassor diameter) more than 5 at the operation of the apparatus in vacuum and more than 7.5 at atmospheric pressure does not influence the desorption effect. When wastewater treatment at pH 6 about 60-85 per cent of suspended solids is removed from the liquid by the apparatus in vacuum.

The experiments showed that foam can be reduced by means of degassing liquid, with water and air mixture (essentialy with foam) as well as with air, being fed to the degassor through the nozzles, located at the appropriate height above the liquid layer. When the nozzles were absent filling of the whole degassor with foam was observed.

The most effect of foam reduction is provided by the operation of the screwed jet. When spraying wastewater through these nozzles, located above the barbotage layer at height of 0.7 m, the desorption of volatile components achieves 60-80 per cent. The presence of suspended solids in the amount of I g/l in the wastewater had no effect upon the wastewater treatment rate. It is necessary to note that the release of suspended solids from the wastewater after its degassing proceeds more quickly, than before treatment. The criterion equations were obtained for the barbotage process in the form of dimensionless criteria of Nusselt, Reynolds and Prandtlja. The Reynold's criterion is defined according to the formula which takes into account the saturation of layer with gas; the formula is the following:

$$Re = \frac{W_{ж} \cdot d_{ср}}{(1-\varphi)\, \mu_{ж}} \qquad 8$$

where $W_{ж} = U.P_{ж}$ – mass liquid rate, kg.sq.m.sec., $\mu_{ж}$ – liquid viscisity, kg.m.sec; $P_{ж}$ –wastewater density kg/m; $d_{ср}$ – air bubble average diameter.

The index has two values - 0.7 and 0.34. the Re value characterizing the transfer is equal to 80.

The criterion equation for the desorption of carbon sulphide at Re ⟨ 80 is the following $Nu = A.\ Re^{0.7}.Pr^{0.5}$ (9) at Re ⟩ 80 $Nu = A.Re^{0.34}.Pr^{0.5}$ (I0) For the desorption of hydrogen sulphide at Re⩽ 80

$$Nu = A.Re.^{0.98}.Pr^{0.5} \qquad (II)$$

The value of coefficient A for the desorption of carbon sulphide for the term, Re ⟨ 80, is equal to 2.3 in vacuum 600mm Hg and 2 mm in vacuum from 200 to 0. For the desorption of hydrogen sulphide they are equal to 0.7 in vacuum 600 Hg and 0.6 in vacuum from 200 to 0.

The A values are also defined for the terms when Re ⟩ 80.

The degassing rate of various types of wastewaters is generally 98-99 per cent (the residual content of the volatile component is 0.4 - I.5 mg/l). In their case the post-treatment of wastewaters from volatile components is not required. In the course of degassing at normal pressure the wastewater saturation with air oxygen takes place in the apparatus that is very significant.

The treatment cost of I cu.m. of wastewater (without considering the utilization of valuable matters and the decrease of the BOD value) in the apparatus, operating in vacuum, is I copeck, but at normal pressure it is 5 copecks. The given cost may be considerably reduced, if the volatile components are the valuable products.

Desorption in the spraying apparatus

The hollow apparatus similar to the nozzle-type desorber is proposed for removing the volatile components from the wastewaters by the liquid spraying process. The desorption in the hollow spraying apparatus is realized at the expense of diffusion of volatile components through the surface of drops at their fall, as well as partially, at the expense of the false bottom operation as a fall-through plate, and insignificantly, at water flow through the inside surface of desorbers. The height of drops fall (up to the false bottom) is 4 m. For liquid spraying various types of nozzles with the I0 mm outlet opening are used. The hollow desorbers operate at the spraying density 12-120 cu.m/sq.m.hr.

When defining the contact surface of phases while spraying the wastewater with the used nozzles (with the I0 mm outlet opening) it is assumed that the average diameter of drops is equal. to I.5 mm. The drop velocity of such a drop is 4.5 m/sec., that significantly exceeds the air velocity at the counter current for the given cases of treatment wastes in the desorber.

Using the known formula for the definition of the contact surface of the phases a = 6 /Wk.d cp and substituting the accepted values in it, we shall obtain for the discussed cases of wastewater treatment the following:

$$a = \frac{I000\,\text{и}}{I.125}$$

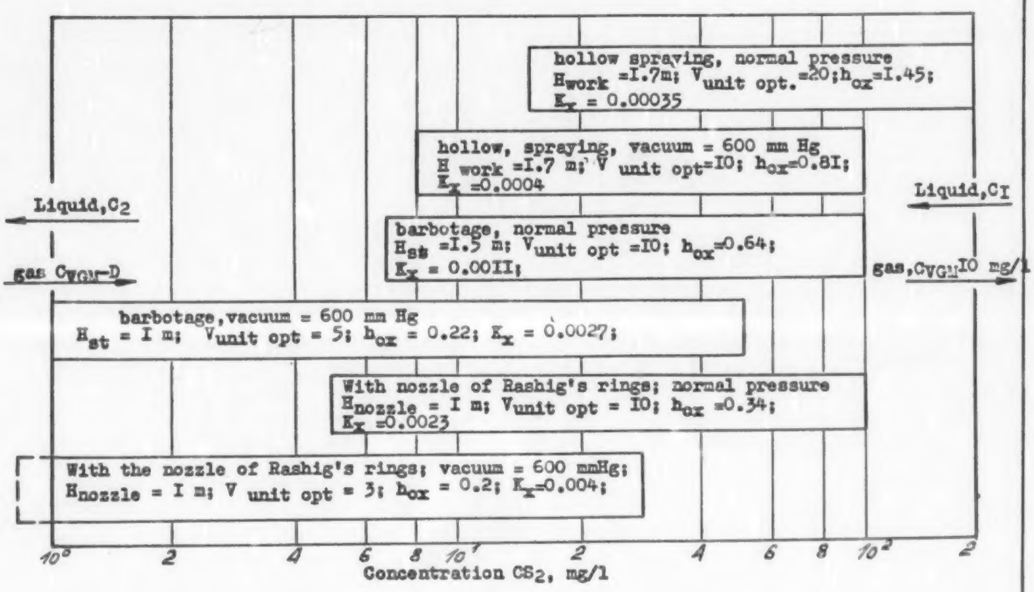
where a - unit contact surface of phases in I cu.m. of hollow spraying apparatus;

и – spraying density, cu.m/sq.m.sec.

The desorber operation results show that the achieved rate of water treatment is 80-85 per cent, but in some cases it is up to 92%.

The mass transfer factor is inversely proportional to the spraying density. It remains practically constant at air consumption more than 800 cu.m./sq.m.hr. (the unit consumption is about 30). When feeding the waste liquid through the perforated pipeline (instead of nozzles) the treatment effect is reduced in 10-15 per cent.

The K_x coefficient is dependent on the vacuum value. It is also increased at the ejector air inlet to the pipeline ahead of the nozzle. The main amount of volatile components (up to 70-80 per cent) is removed from the


hollow spraying, normal pressure
H_{work} =I.7m; $V_{unit\ opt.}$=20; h_{ox}=I.45;
K_x = 0.00035
hollow, spraying, vacuum = 600 mm Hg
H work =I.7 m; V unit opt=I0; h_{ox}=0.8I;
K_x =0.0004
Liquid, C_I
Liquid, C_2
barbotage, normal pressure
H_{st} =I.5 m; $V_{unit\ opt}$ =I0; h_{ox}=0.64;
K_x = 0.00II;
gas C_{VGM}-D
gas, C_{VGM} I0 mg/l
barbotage, vacuum = 600 mm Hg
H_{st} = I m; $V_{unit\ opt}$ = 5; h_{ox} = 0.22; K_x = 0.0027;
With nozzle of Rashig's rings; normal pressure
H_{nozzle} = I m; $V_{unit\ opt}$ = I0; h_{ox} =0.34;
K_x =0.0023
With the nozzle of Rashig's rings; vacuum = 600 mmHg;
H_{nozzle} = I m; V unit opt = 3; h_{ox} = 0.2; K_x=0.004;
10^0
2
4
6
8
10^1
2
4
6
8
10^2
2
Concentration CS_2, mg/l

Application field of various type degassors wastewater when the drops are falling at the distance of 0.7-I m from the nozzle.

The optimum pressure ahead of the nozzle is a liquid head equal to 0.7 - I atm. On the basis of generalization of the operation data on the plant-scale and full-scale hollow spraying-type apparatus the criterion equation is obtained for the desorption process of carbon sulphide from wastewaters.

$$N_u = A.Re^{-0.16}.Pr^{0.5}$$

where A - for vacuum 600 m. Hg - 400, for vacuum 200 mm Hg - 250, for normal pressure - 200 mm Hg. In the criteria of Nussolt and Reynolds average drop diameter is accepted for the typical dimension. Since the lower concentrated mixture is formed in the spraying desorber the cost of valuable components as returned to the manufacture will be higher than for the nozzle-type and the barbotage-type apparatus.

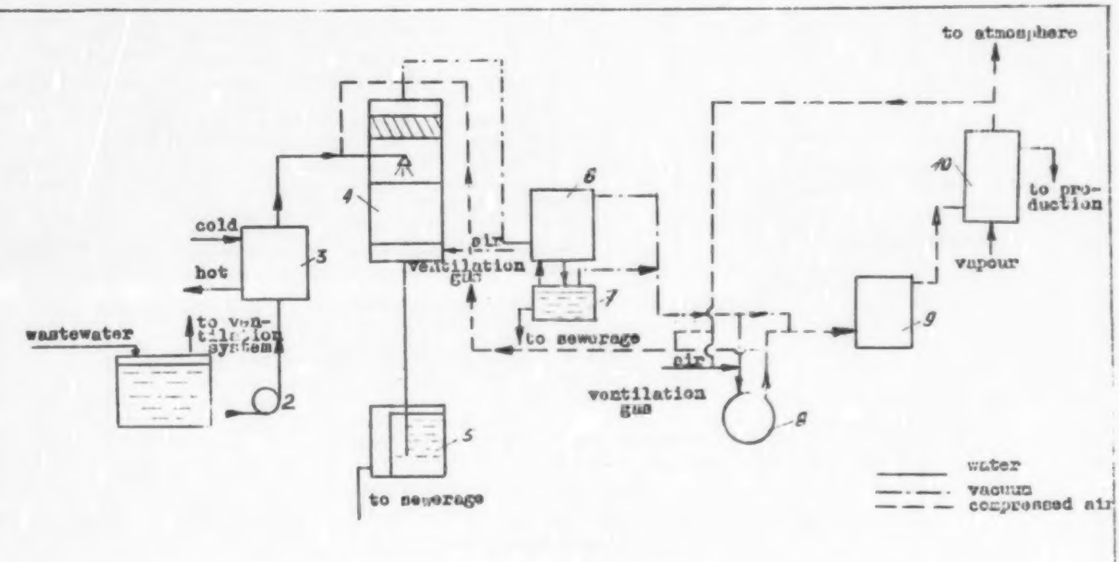
When generalizing the performance results of the nozzle-type desorbers of Rashig's rings with barbotage layer of liquid and hollow sprayer-type ones, it is necessary to note that these data allow to compare the discussed desorbers as to the achieved efficiency of the wastewater disinfection, they afford the opportunity to perform the process design of these facilities and to recommend them for wastewater treatment practice from various industries. In the above-mentioned desorbers the waste liquid depth (under otherwise equal conditions) is clearly shown in the figure 2. The selection of the wastewater treatment process is performed depending on the local conditions. The discussed methods of desorption and designing apparatuses have recently found the application in chemical, pulp and paper and food industries. The schematic diagram of one of industrial installations is given in the figure 3. The performance of this installation provides for the high-rate treatment of water and vapour and gas mixture. In addition the return of valuable substances takes place.

The application field of various types of desorbers is being expanded with the increase of requirements to the sanitary protection of waters and atmosphere from gas emission contaminations.

List of inscriptions to figures

Figure I. Barbotage-type degassor: I,4 - water supply pipeline; 2 - spraying nozzles; 3 - barbotage liquid layer; 5 - removable barbotage unit; 6 - drop removing layer; 7 - pipeline for vapour and gas mixture outlet; 8 - explosion-proof device; 9 - pipeline for treated water outlet; I0 - vat for separation micro bubbles from liquid; I-I3 - Pipelines for outlet from the apparatus; I2 - Hydraulic vat.

Figure 2. Application field of various type degassors. Spraying density = 12 cu.m/sq.m.hr, t = 60°C; spraying device - controllable cylindrical nozzle (C.C.N.); concentration of carbon sulphide in the vapour and gas mixture CVGM = 100 mg/1; mass transfer factor = K_x kilomole/sq.m.sec; concentration of carbon sulphide in water, C_I - at the apparatus inlet, C_2 - at the apparatus outlet; H nozzle - height of the nozzle, h_{ox} - unit



Shematic diagram of industrial desorption installation transfer height; U unit opt. - unit air consumption.

Figure 3. Schematic diagram of industrial installation for desorption of carbon sulphide, hydrogen sulphide with carbon sulphide recovery.

1. Water intake tank; 2 - pump; 3 - heat exchanger; 4 - degassor; 5 - hydraulic gate valve (barometric vat); 6 - cooler; 7 - condensate collector; 8 - vacuum pump; 9 - Adsorber for hydrogen sulphide; 10 - adsorber for carbon sulphide;

2. Hollow, spraying, vacuum = 600 mm Hg H work = 1.7 m; V unit opt. = 10; $h_{ox} = 0.81$; $K_x = 0.004$
3. barbotage, normal pressure $H_{st} = 1.5$ m; V unit opt. = 10; $h_{ox} = 0.64$; $K_x = 0.0011$
4. barbotage, vacuum = 600 mm Hg Hst = 1 m; V unit opt. = 5; $h_{ox} = 0.22$; $K_x = 0.0027$;
5. With nozzle of Rashigs rings, normal pressure H nozzle = 1 m; V unit opt. = 10; $h_{ox} = 0.34$; $K_x = 0.0023$
6. With the nozzle of Rashig's rings; vacuum = 60 mm Hg; H nozzle = 1 m; V unit opt. = 3; $h_{ox} = 0.2$; $K_x = 0.004$;

DESIGN OF FACILITIES FOR PHYSICAL– CHEMICAL TREATMENT OF RAW WASTEWATER

Presented by Gordon L. Culp at Technology Transfer Seminars
Sponsored by the U.S. Environmental Protection Agency.

INTRODUCTION

The various approaches to physical-chemical treatment of raw wastewater as described by other speakers in this session, all involve the use of the same basic unit processes of coagulation and settling for removal of suspended solids and, in some cases, phosphorus; the use of filtration for further removals of suspended solids and phosphorus; and carbon adsorption for removal of soluble organics.

This paper will discuss: typical design parameters for the unit processes involved in physical-chemical treatment of raw wastes; how the design engineer may determine the design criteria best suited for a given wastewater; criteria being used for full-scale plants; and the results obtained in studies in several locales.

PLANT PERFORMANCE SPECIFICATIONS

For purposes of providing an illustrative example for discussion of design considerations, the raw waste characteristics and effluent requirements shown in Table 1 have been assumed. The effluent standards cannot be met with secondary treatment alone as chemical coagulation would be required to meet the phosphorus standards and, at least, filtration of a secondary effluent to meet the BOD and SS requirements. On the other hand, the effluent standards are not so stringent to know for certain that physical-chemical techniques must be used in series with biological treatment. Therefore, a design engineer faced with the above situation should conduct the necessary tests to determine if the above standards could be met by physical-chemical treatment alone, and if so, what design criteria should be used. The unit processes involved are proven to the degree that extensive, on-site pilot tests are not necessary for most wastewaters and design criteria can be obtained in laboratory tests. Of course, if time and funds permit, an on-site pilot test over several months will permit an even more accurate determination of design criteria under a wider variety of operating conditions. Should on-site pilot studies be considered, the scale of the equipment can be tailored to meet the individual needs of the project. Small diameter filters and carbon columns (about 6-inch diameter) are adequate for column studies and can often be obtained from suppliers of carbon and filter manufacturers on a loan or rental basis. Pilot clarifiers of 6-10 feet in diameter can usually be rented from clarifier manufacturers. In a like manner, pilot sludge thickening and dewatering equipment can also be rented. The overall cost of pilot studies will vary widely depending upon the extent of the data collected. A meaningful study should span several months if any seasonal variations in raw wastewater quality are anticipated. Although pilot studies unquestionably provide a firmer basis of design, the author's experiences indicate that, except in unusual circumstances, the design criteria for the physical-chemical unit processes under consideration here can be determined with suitable accuracy in properly conducted laboratory tests on representative raw waste samples.

TABLE 1

WASTEWATER CHARACTERISTICS AND EFFLUENT QUALITY REQUIREMENTS

	Influent, Average (mg/1)	Effluent, weekly Average (mg/1)
BOD	180	15
COD	520	30
Suspended Solids	250	10
Hardness, as $CaCO_3$	150	–
Phosphorus	11.5	1
Alkalinity	220	–

PRELIMINARY DATA COLLECTION

In order to proceed with the design on a rational basis, a characterization of the raw wastewater in terms of its amenability to physical-chemical treatment must be made. The following description of tests on wastewater illustrates techniques which may be used. Four 24-hour composite samples collected during four different weeks are used in the example.

The goals of these tests are to answer the following major questions which must be answered before the design can proceed:

- What is the best coagulant?
- How much sludge is produced?
- How well does the sludge dewater?
- Is coagulant recovery practical?
- What is the nonadsorbable fraction of organics in the raw wastewater?
- How much carbon contact time will be required?
- What effluent quality can be expected?

SELECTION OF COAGULANT

There are four major classes of coagulants which may be considered singularly or in combination:

1. **Polymers.** Some investigators have reported successful coagulation of raw sewage with polymers alone. The author has examined polymers as the primary coagulant on many wastewaters without finding them economically attractive when compared to the inorganic coagulants available. The cost of polymers is $1-$2 per pound. When used as the primary coagulant, polymers do not provide phosphorus removal. One of the following inorganic coagulants is required if phosphorus removal is of concern. Polymers used in conjunction with an inorganic coagulant are effective settling and filtration aids.

2. **Iron Salts.** Ferric chloride or ferric sulfate may be used for both suspended solids and phosphorus removal. Experience has shown that efficient phosphorus removal requires the stoichiometric amount of iron (1.8 mg/1 Fe per mg/1 of P) to be supplemented by at least 10 mg/1 of iron for hydroxide formation. Typically, 15-30 mg/1 as Fe is required to provide phosphorus reductions of 85-90 per cent. When considering iron for coagulation of raw wastes, it must be remembered that in an anaerobic environment, as may be encountered in a downstream carbon column, iron sulfide may be formed. This black precipitate is obviously not desirable in the final effluent.

3. **Aluminum Salts.** Both aluminum sulfate (alum) and sodium aluminate have been used for coagulation of wastewaters. Alum is generally a much more effective coagulant than sodium aluminate. Alum doses of 200-300 mg/1 are typically required for 85-90 percent phosphorus removal (an aluminum to phosphorus ratio of 2-3). Disadvantages of both the iron and aluminum salts are (1) both form gelatinous hydroxide flocs which are difficult to dewater in many cases; (2) no techniques are available for recovery and reuse of the coagulant when phosphorus removal is required; and (3) large amounts of ions (chlorides or sulfates) are added to the wastewater.

4. **Lime.** Lime has been successfully used in several locales for wastewater coagulation and phosphorus removal. The amount of lime required is independent of the amount of phosphorus present; rather, it is a function of the wastewater alkalinity and hardness. When the pH reaches 9.5 due to the addition of lime, the orthophosphate is converted to an insoluble form. In some cases, additional quantities of lime may be required to form a readily settable floc. Lime has been recalcined and reused in some cases when used to coagulate secondary effluent. However, as will be illustrated later, recalcining and reuse may often not be practical when it is used to coagulate raw wastewaters due to the large amount of inert materials present in the combined raw sewage-chemical sludges. In any case, lime sludges usually dewater more readily than those resulting from iron or aluminum coagulation.

The choice of coagulant can usually be made rather quickly by laboratory jar tests. The following illustrative example is based on data collected on a raw wastewater from a community in the Midwest.

In the technique used, six one-liter samples are dosed with the coagulants being studied while being rapidly mixed with a jar test device. In this example, 0.5 mg/l of an anionic polymer (nopcofloc 930, manufactured by Diamond Shamrock) was added as a settling aid. Following a 60-second rapid mix, the samples are slowly mixed for about 5 minutes. These are then allowed to stand quiecently to permit settling of the floc. Samples of the supernatant are then obtained with a pipette from a point just below the liquid surface in the jar. This is done to avoid including any of the floating solids which are invariably found in raw sewage. This supernatant sample is then analyzed for turbidity, pH, hardness (when lime is used as a coagulant), and phosphorus. A portion of the remaining supernatant is filtered through a Whatman No. 2 filter paper. The filtrate is analyzed for turbidity, phosphorus, and in some cases, TOC, COD, BOD and suspended solids. Past experience has shown that the filtrate quality obtained with this filter paper will be about the same as that which will be achieved with a mixed-media filter.

Lime Coagulation

By plotting the jar test data, it was determined that the lime dosages required to achieve a filtrate phosphorus concentration of one mg/l were as follows:

Sample No. 1 = 132 mg/l as $Ca(OH)_2$
Sample No. 2 = 100 mg/l as $Ca(OH)_2$
Sample No. 3 = 110 mg/l as $Ca(OH)_2$
Sample No. 4 = 130 mg/l as $Ca(OH)_2$

One mg/l phosphorus was achieved at a pH of 9.1-9.5. The lime dosage required for optimum solids removal varied from 100-130 mg/l. In general, a somewhat higher dose of lime was required for optimum solids removal than was required for phosphorus removal. A lime dose of 200 mg/l achieved adequate solids removal for all four samples and this dose will be used in subsequent calculation of the cost of lime coagulation.

Suspended solids analyses showed that settled supernatant contained less than 5 mg/l suspended solids at this dose and the filtered supernatant generally contained no measurable suspended solids. A lime dose of 200 mg/l results in an effluent phosphorus concentration of 0.07-0.26 mg/l and a pH of 9.6-10.1. The lime and polymer dosage produced a rapidly settling floc, as it does in most wastewaters.

Alum Coagulation

The alum dosages required to achieve a filtrate phosphorus concentration of one mg/l were as follows:

Sample No. 1 = 120 mg/l
Sample No. 2 = 153 mg/l
Sample No. 3 = 165 mg/l
Sample No. 4 = 150 mg/l

The pH was reduced to 6.7-7.1 by the above alum dosages.

Adequate solids removal was achieved at alum doses equal to or less than that required for phosphorus removal.

Iron Coagulation

The ferric chloride dosages required to achieve a filtrate phosphorus concentration of one mg/l were as follows:

Sample No. 1 = 20 mg/l as Fe
Sample No. 3 = 27 mg/l as Fe
Sample No. 4 = 23 mg/l as Fe

The required Fe/P ratios were 2.7, 2.4, and 2.5 respectively. It appeared that the dose required for phosphorus removal would equal or exceed that required for solids removal.

Comparison of Coagulant Costs

The cost of the various coagulants at the plant site is as follows:

Lime = $16.75/ton of CaO
Alum = $70/ton
Ferric Chloride = $90/ton (or $262/ton of Fe)

The estimated costs for coagulation with the following doses are as follows:

200 mg/l lime [as $Ca(OH)_2$] = $10.60/mg
160 mg/l alum = $46.50/mg
23 mg/l Fe = $25.10/mg

It is apparent that lime is the lowest cost coagulant, even when the lime dosage involved reduces the phosphorus to less than 0.3 mg/l.

Of course, the total economic comparison must also include the relative cost of sludge disposal associated with each coagulant. Nearly always the lime sludges may be disposed of at significantly lower costs than the sludges resulting from either alum or iron coagulation. Thus, in the above example, there is little doubt that lime will remain the most economical coagulant when sludge disposal costs are included.

The general dewatering characteristics of the sludge may be determined by laboratory tests. A 100 ml sludge sample is dewatered with a Whatman No. 2 filter paper in a Buchner funnel with laboratory vacuum. The volume of filtrate versus time is then plotted and compared to similar data for sludges for which field experience has also been obtained. Figure 1 presents an example comparison which shows that the sludges resulting from coagulation of this wastewater dewatered even more readily in the lab than did another sludge which later proved to dewater very well in a centrifuge. Thus, the dewatering of the sludge does not appear to be a limiting factor in this case.

It is difficult to obtain an accurate gravimetric measurement of sludge quantities in a laboratory test due to loss of solids during decanting, etc. However, it is possible to estimate the quantities of lime sludge from the chemistry involved and the data collected from the jar tests. As shown in Table 2, about 4,050 pounds of solids per million gallons would be expected with a lime dose of 200 mg/l. Following incineration, the ash quantities would be about 2,165 pounds per million gallons.

With this information, it is then possible to determine the feasibility of recalcining and reusing the lime. From Table 2, it is apparent that if one were to recycle all of 820 pounds of the lime recovered per mg, that one would also recycle 1,345 pounds of inert ashes. Assuming that a 20 percent blowdown were practiced, one would recycle 670 pounds lime and 1,080 pounds inerts. After the second cycle, there would not be 1,345 + 1,080 pounds of inerts in the furnace discharge or 2,425 pounds of inerts. Table 3 presents an illustrative calculation of the buildup of inerts through 11 cycles with 20 percent blowdown of the furnace product.

Eventually, one will be dewatering and incinerating about 6,500 pounds of inerts per mg in order to recover only 670 pounds of lime. The solids handling system would have to be sized for a solids load corresponding to a nonvolatile fraction of about 7,300 pounds/mg rather than the 2,165 pounds/mg if the sludge was merely incinerated and thrown away. One would be spending far more to recover the lime than it would be worth. A higher blowdown rate still does not make recalcining practical in this example. It is far cheaper to use the lime once and dispose of the sludge. Until a means is available for very efficient separation of lime from the inerts in the combined raw sewage-chemical sludge, lime recycle will often not be practical when coagulating raw sewage unless very high lime doses are involved. Envirotech is developing a dry classification technique for this purpose

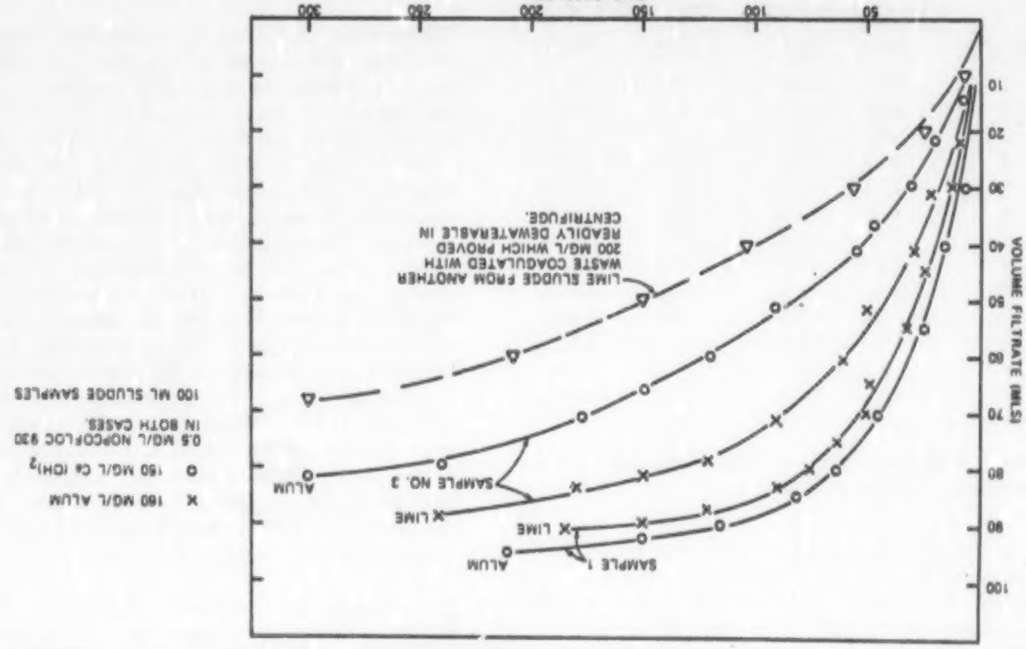


FIGURE 1

SLUDGE DEWATERING CHARACTERISTICS

TABLE 2
ESTIMATE OF LIME SLUDGE QUANTITIES

Raw Sewage Suspended Solids = 250 mg/1
Raw Sewage PO_4 = 34.5 mg/1
Add 200 mg/1 lime as $Ca(OH)_2$ or 108 mg/1 Ca
Assume all 250 mg/1 raw sewage SS removed
Assume lime reacts with PO_4 to form
$Ca_5(OH)\ (PO_4)_3$
Weight of $Ca_5(OH)\ (PO_4)_3$ formed =

$$\frac{Ca_5(OH)\ (PO_4)_3 \text{ m.w.}}{(OP_4)_3 \text{ m.w.}} \times PO_4 \text{ conc} = \frac{502}{285} \times 34.5 = 61 \text{ mg/1}$$

Raw Hardness = 150 mg/1 as $CaCO_3$ [as measured on Sample No. 4 with 200 mg/1 $Ca(OH)_2$]

Treated Hardness = 185 mg/1 as $CaCO_3$

Ca lost in effluent $= \frac{40}{100} \times (185-150) = 14$ mg/1

Ca in $Ca_5(OH)\ (PO_4)_3 = \frac{200}{502} \times 61$ mg/1 $= 24$ mg/1

Ca in $CaCO_3$ sludge $= 108 - (24 + 14) = 70$ mg/1

Quantity of $CaCO_3 = \frac{100}{40} \times 70 = 175$ mg/1

Sludge Composition

Raw sewage Solids	=	250 mg/1	=	2080 lbs/mg	x	.4	=	835 lbs/mg
$Ca_5(OH)\ (PO_4)_3$	=	61 mg/1	=	510 lbs/mg	x	1.0	=	510 lbs/mg
$CaCO_3$	=	175 mg/1	=	1460 lbs/mg	x	.56	=	820 lbs/mg
				4050 lbs/mg				2165 lbs/mg

TABLE 3
EFFECT OF RECYCLING RECALCINED MATERIALS

	Pounds per Million Gallons			
	Furnace Discharge		Recycled Material with 20% Blowdown	
Cycle No.	Lime	Inerts	Lime	Inerts
1	820	1345	670	1080
2	820	2425	670	1940
3	820	3285	670	2630
4	820	3975	670	3180
5	820	4525	670	3620
6	820	4965	670	3970
7	820	5315	670	4250
8	820	5595	670	4480
9	820	5825	670	4660
10	820	6005	670	4800
11	820	6145	670	4915
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—

Assumes 100% calcium recovery from sludge and makeup lime to maintain 200 mg/1 lime dose

but no operational data are yet available. A plant under construction in Contra Costa, California will make use of this dry classification technique on sludges resulting from lime coagulation of raw sewage.

CARBON ADSORPTION

There are organics (i.e., sugars) which may be readily biodegradable but which are difficult to adsorb on carbon. The amount of these nonadsorbable materials will vary greatly from wastewater to wastewater and their presence will be the governing factor concerning the quality of effluent which can be achieved by carbon adsorption. The same physical-chemical process may produce a BOD of 10 mg/l in one locale and 30 mg/l in another due to this fact. The ability to remove the soluble organics may be measured in the laboratory by two methods.

One of these methods is a batch process in a beaker while the other is a flow-through, carbon column experiment. In the first case, the raw sewage is contacted with 1,000 mg/l of Aqua Nuchar A, a powdered carbon, for one hour. Alternately, a sample of the granular carbon under consideration may be ground and applied to the sample. The sample is then coagulated, settled and the supernatant filtered through Whatman No. 2 filter paper prior to analysis. Past work done with powdered carbon indicates that an Aqua Nuchar dose of 600 mg/l and a contact time of five minutes is generally adequate for removal of all adsorbable organics. Thus, the above conditions insure that all adsorbable materials are, in fact, removed. The above technique is a quick method of determining the nonadsorbable fraction of organics. The isotherm technique described by other speakers in this session will provide more information.

The column test may be conducted using Calgon Filtrasorb 400 carbon or equivalent in five ¾-inch diameter columns in series. The columns are sized so that cumulative contact times of 7.5, 15, 30, 45 and 60 minutes are provided at the end of the respective columns. Four to five gallons of raw sewage are coagulated with either lime or alum, settled, the supernatant decanted (the pH adjusted to 7 when lime is used), and the clarified wastewater pumped through the columns. This quantity of sewage will provide several days of operation in columns of this size. The tests should be continued as long as possible to accurately determine the effects of biological activity. The sludge should be saved for analysis. The results from these small columns have been found by the author to be consistent with those obtained in larger units. For example, in one study spanning several months, the results concerning contact time from small laboratory columns in the first four weeks of the study were essentially the same observed from both 6-inch diameter and 3-foot diameter columns operated over several months.

The reasons for preferably conducting both the powdered carbon and column tests are to determine if the effluent from the columns could be lower in BOD than that achieved by adsorption alone due to the biological growth in a column and to determine the effects of contact time on column performance.

Powdered Carbon Results

The effluent quality achieved by the powdered carbon technique above should closely represent the non-adsorbable fraction of the organics contained in the raw waste sample tested. The results obtained with the wastewater in question are as follows:

The three parameters show similar trends from sample to sample, with the fourth sample containing substantially less nonadsorbable organics than Samples 2 and 3 and somewhat less than Sample 1. It appears that the BOD of 2 mg/l measured for Sample 4 may be low as the COD/BOD ratio is considerably out of line with the other samples. The COD appears valid as the COD/TOC ratio compares closely with the other samples. However, it is possible that there was a change in the nature of the unadsorbable organics so that, in fact, a smaller portion was biodegradable.

The nonadsorbable BOD ranged from 2-18 mg/l with an average of 12.2 mg/l for the four samples.

Column Tests

Figures 2 and 3 summarize the data collected from the laboratory columns. As can be seen from the figures, the benefits achieved by contact times greater than 30 minutes are slight. The carbon column effluent BOD values after 60 minutes contact ranged from 5 to 15 mg/l and averaged 11.0 mg/l. The BOD samples collected at a 30-minute contact time averaged 12.5 mg/l.

An estimate of the required carbon dosage can be made by assuming that carbon will be withdrawn for regeneration when the carbon loading is 0.5 pounds of COD removed per pound of carbon. This loading has

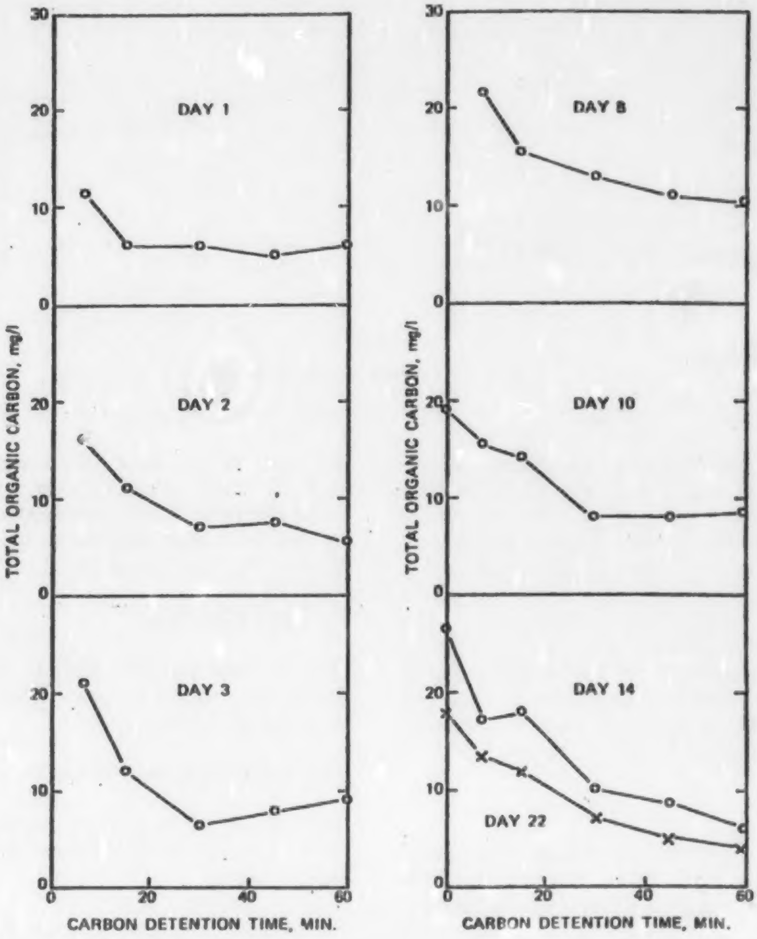


FIGURE 2

PILOT CARBON COLUMN DATA

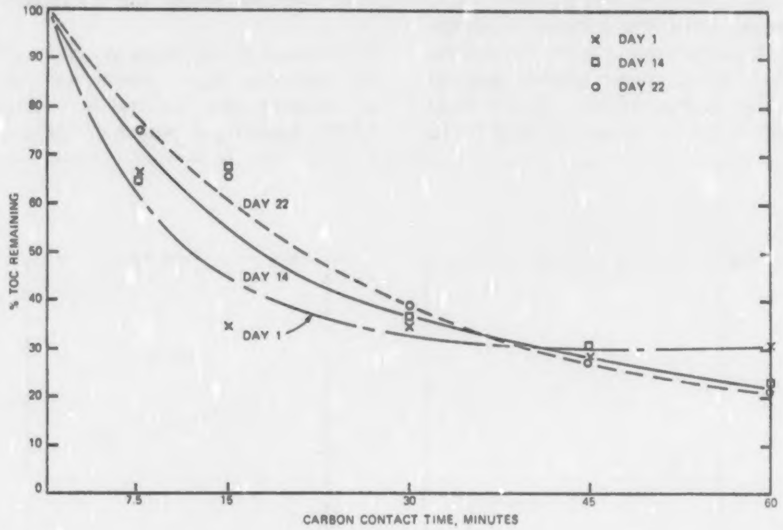


FIGURE 3

PILOT CARBON COLUMN DATA

been achieved in several studies. An average soluble influent COD of 86 mg/l was achieved with lime clarification in the four series of jar tests. The average COD achieved in the four powdered carbon tests was 23 mg/l and averaged 24 mg/l after 30 minutes contact in the columns. Thus, an average COD removal of about 62 mg/l would be expected from these tests. The corresponding carbon dosage is 1,030 pounds/mg. Carbon dosages calculated from short-term laboratory column tests are usually conservatively high, as biological action usually results in greater permissible loadings in a continuous, plant scale operation.

PROCESS DESIGN

The purpose of this section is to discuss those design criteria necessary for plant design. Figure 4 illustrates the flow sheet upon which the following discussion is based.

Flow

Both the average and peak flows are of concern. In a physical-chemical plant, there is a substantial volume of flow recycled to the head of the plant from the following major sources: (1) furnace scrubber underflow, (2) filter and activated carbon backwash flows, (3) sludge thickener overflow, and (4) sludge dewatering filtrate or centrate. For example, a 15 mgd average flow rate may be associated with a peak hourly rate of 30 mgd. To these values must be added the volume of recycle streams. If these recycle streams total 3.5 mgd in the above example, then the design hydraulic flow rates become 18.5 mgd average and 33.5 mgd peak hour.

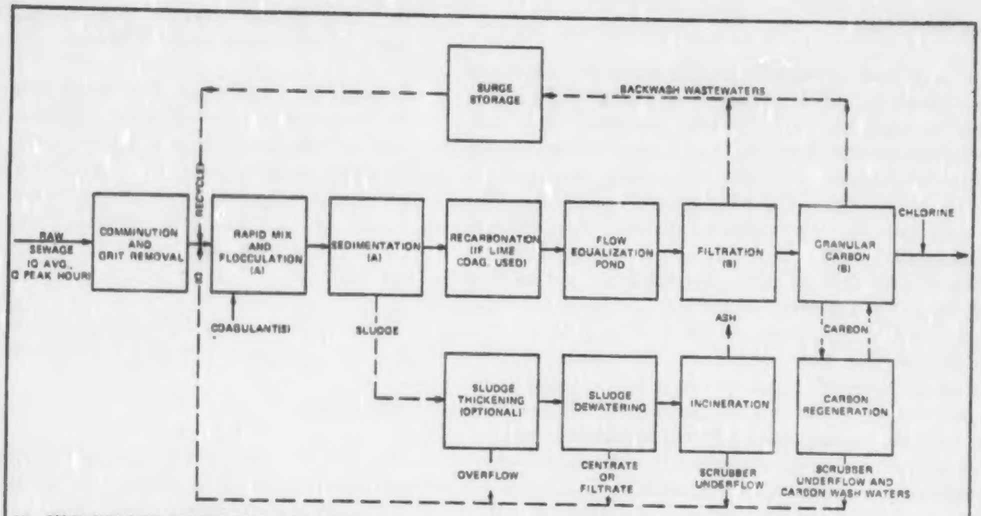
Preliminary Treatment

Comminution and grit removal facilities designed in accordance with standard sewage treatment design practices should be provided.

Chemical Feed, Rapid Mix and Flocculation

These functions may all be carried out in accordance with standard practices followed in the water treatment field for years.

Proper rapid mixing is important to efficient utilization of the coagulating chemicals. The use of a mechanical rapid mixing device in the basins with a total of 2 minutes detention time of the average flow is recommended. When using lime as coagulant, scaling of the mixer shaft will occur and may cause excessive bearing wear if not cleaned regularly. In any case, provision of two parallel rapid mixing units each with a nominal capacity of one-half the design flow is prudent to provide flexibility in operation. Should one mixing unit be down for repair, the entire flow can be passed


SURGE STORAGE
BACKWASH WASTEWATERS
RECYCLE
Q
RAW SEWAGE (Q AVG., Q PEAK HOUR)
COMMINUTION AND GRIT REMOVAL
RAPID MIX AND FLOCCULATION (A)
SEDIMENTATION (A)
RECARBONATION (IF LIME COAG. USED)
FLOW EQUALIZATION POND
FILTRATION (B)
GRANULAR CARBON (B)
CHLORINE
COAGULANT(S)
SLUDGE
ASH
CARBON
SLUDGE THICKENING (OPTIONAL)
SLUDGE DEWATERING
INCINERATION
CARBON REGENERATION
OVERFLOW
CENTRATE OR FILTRATE
SCRUBBER UNDERFLOW
SCRUBBER UNDERFLOW AND CARBON WASH WATERS

(A) DESIGN FLOW BASED ON Q PEAK HOUR PLUS Q RECYCLE.
(B) DESIGN FLOW BASED ON Q AVERAGE PLUS Q RECYCLE.

FIGURE 4

ILLUSTRATIVE SCHEMATIC OF
A PHYSICAL – CHEMICAL TREATMENT PLANT

through the remaining basin which will still provide one minute mixing with the above criteria.

A mechanically mixed flocculator with 15 minutes detention is generally adequate for wastewaters. In many cases, the flocculation resulting from the large coagulant doses added to wastewaters results in very rapid flocculation and even shorter detention times may be feasible. Provisions should be made to add up to one mg/l polymer at the rapid mix or at the flocculator inlet or outlet or split among these points.

Clarifier Sizing

The critical design parameter is the peak hourly surface overflow rate. Gross carryover of solids can cause the downstream filter or adsorption processes to fail due to excessive headloss which, in turn, will result in a total failure of the plant. Thus, it is of little consolation to know the clarifier will perform properly under average flow conditions only to have a carryover of excessive solids during the peak hourly flow shut the entire plant down. A maximum peak hourly rate of 1,400 gpd/ft^2 for conventional horizontal or radial flow clarifiers is recommended when using lime as a coagulant unless pilot tests indicate that other rates should be used. A maximum average rate of 900 gpd/ft^2 is recommended. Whichever of these two criteria results in the larger clarifier size should be used.

Several attempts have been made to use upflow, sludge blanket type clarifiers on coagulated primary or secondary effluents. Difficulty in holding a sludge blanket has been reported in every case. Successful operation has been achieved with these units by lowering the overflow rate to conventional clarifier rates and eliminating the sludge blanket, which in essence, converts the unit to a conventional radial flow basin. The instability of the sludge blanket or solids contact units is due to the organics found in the raw sewage and the wide variations in incoming flow. These units have been most successful in treating groundwaters of uniform composition at a constant flow rate. The author does not recommend their use on coagulated wastewaters.

Provision should be made for recirculation of controlled amounts of sludge from the bottom of the clarifier to the rapid mix inlet. The high pH of lime-treated water will form deposits of calcium carbonate on structures and in pipelines which it contacts. Lime sludge suction lines should be glass lined to facilitate cleaning. Provisions must also be made for regular cleaning of all other pipelines which carry the high pH effluent. Use of the new polyurethane cleaning pigs should be compatible with the layout of the pipelines. Mechanical sludge collection equipment used in lime settling basins should be of the bottom scraper type rather than the vacuum pickup style because of the dense sludge to be handled.

Recarbonation

Lime treatment of wastewaters for phosphorus removal often raises the pH to values of 10-11. At this pH, the water is unstable and calcium carbonate floc will precipitate readily. This floc is very tenacious and would encrust any downstream filters or carbon particles to a serious degree. The pH may be lowered by injecting CO_2 gas obtained from the incinerator stack gases. Primary recarbonation is used to reduce the pH from 11 to 9.3, which is near that of minimum solubility for calcium carbonate. In domestic wastewater, primary recarbonation to pH = 9.3 results in the formation of a heavy, rapidly settling floc which is principally calcium carbonate, although some phosphorus is also removed from solution by adsorption on the floc. If sufficient reaction time, usually about 15 minutes in cold water, is allowed for the primary recarbonation reaction to go to completion, for the calcium carbonate floc does not redissolve with subsequent further lowering of pH in secondary recarbonation. If lime is to be reclaimed by recalcining and reused, this settled primary recarbonation floc is a rich source of calcium oxide, and may represent as much as one third of the total recoverable lime. If the pH were not reduced to less than about 8.8 before application to the filters and carbon beds, extensive deposition of calcium carbonate would occur on the surface of the grains. This could reduce filter efficiency, and could also drastically reduce the adsorptive capacity of granular activated carbon for organics. It would produce rapid ash buildup in the carbon pores upon regeneration of the carbon, and would lead to early replacement of the carbon.

It is possible to reduce the pH of a treated wastewater from 11 to 7 or to any other desired value in one stage of recarbonation. Single-stage recarbonation eliminates the need for the intermediate settling basin which is used with two-stage systems. However, by applying sufficient carbon dioxide in one step for the total pH reduction, little, if any, calcium is precipitated with the bulk of calcium remaining in solution, thus increasing the calcium hardness of the finished water, and, in addition, causing the loss of a large quantity of calcium carbonate which could otherwise be settled out, recalcined to lime, and reused. If lime is to be reclaimed or if calcium reduction in the effluent is desired, then two-stage recarbonation is required. Otherwise, single-stage recarbonation may be used with a substantial savings in initial cost, and a reduction in the amount of lime sludge to be handled.

In our example wastewater discussed earlier, there would be no need for two-stage recarbonation because (1) no reuse of lime is planned, (2) the phosphorus goals can be achieved without the slight additional phosphorus which may be provided by two-stage recarbonation, and (3) the low lime dosage required does not add a significant quantity of calcium to the effluent.

If two-stage recarbonation is being considered only for the purposes of lime recovery, one should compare the value of the lime recovered against the cost of providing two-stage recarbonation. Peak hourly overflow rates for the intermediate clarifier in two-stage recarbonation should not exceed 1,400 gpd/ft^2. Provision should be made for polymer addition to the intermediate clarifier influent.

The details of design for recarbonation systems may be found in *Advanced Wastewater Treatment.*

Filtration

Whether or not filtration is needed prior to activated carbon adsorption is subject to debate. There is no question that filtration ahead of a downflow granular carbon adsorption bed will reduce the rate at which the pores of the activated carbon become plugged with inert materials. Also, the use of an efficient filter permits downstream use of upflow, packed carbon beds which may be operated in the more efficient countercurrent mode discussed later. The question is whether or not the cost of providing the filtration exceeds the benefits mentioned above. Only long-term operating data from plants using granular carbon with and without prior filtration will answer this question. In the interim, a conservative design will include filtration prior to carbon adsorption. In addition to protecting carbon pores from plugging by inerts, mixed media filtration also provides a more efficient means of solids removal than carbon alone, resulting in a higher effluent quality. Filtration Equipment is available which will provide simple, reliable and automatic operation. Carbon is not a particularly effective filter because it acts as basically a surface type filter and as such, is subject to all the shortcomings of other surface filters applied to wastewaters. Any high solids loading will blind a surface type filter in short order. The use of dual media or mixed, tri-media filters provides a much more efficient filtration device which is capable of tolerating a much higher solids loading than is a surface type filter. A discussion of alternate filtration devices and a detailed discussion of filter system design may be found in *Advanced Wastewater Treatment*.

In instances where an upflow expanded bed carbon contactor is used, the filter may be located downstream of the carbon column to remove the bacterial floc which is flushed from the carbon.

It is desirable to precede the filtration step with a flow equalization pond so that the filters may be operated at essentially a constant rate. Provisions should be made for a feed of polymer directly to the filter influent as a filter aid. Filter effluent turbidity and head loss should be monitored continuously with high filter head loss being used to initiate an automated backwash program.

Granular Carbon Adsorption

Because of the unproven economics of recovery and reuse of powdered carbon, the use of granular carbon is the only current practical technique available for removal of soluble organics from coagulated raw wastewater. Chemical oxidation techniques are not yet practical for the large quantities of organics involved. The major design decisions facing the engineer is the selection of a contact time (30 minutes in the example discussed earlier), what dose of carbon is required (can be conservatively estimated by assuming a removal of 0.5 pounds of COD per pound of carbon prior to regeneration) and the configuration of carbon contactor to be used. Typically, the carbon doses will be substantially higher than when granular carbon is applied to coagulated and filtered secondary effluent. In the earlier example, a carbon dose of slightly more than 1,000 pounds per million gallons was estimated. This magnitude of dose is not unusual when applying carbon to coagulated raw sewage.

Contact time of about 30 minutes has been reported by many investigators as marking the point of diminishing returns. That is, a drastically longer contact time would not provide any proportionately greater removal of organics.

The two major alternate contactor configurations to consider are open concrete vessels of either an upflow or downflow type or upflow, countercurrent columns in steel or concrete vessels. The countercurrent approach (see Figure 5) offers a more efficient utilization of the carbon as only the most saturated carbon is withdrawn for generation. This result is aided by the fact that as the carbon becomes saturated with organics, it becomes heavier. When the carbon column is backwashed, the

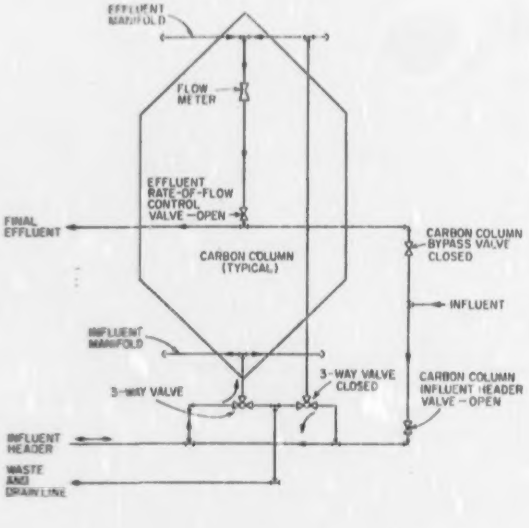

EFFLUENT MANIFOLD
FLOW METER
EFFLUENT RATE-OF-FLOW CONTROL VALVE – OPEN
FINAL EFFLUENT
CARBON COLUMN (TYPICAL)
CARBON COLUMN BYPASS VALVE CLOSED
INFLUENT
INFLUENT MANIFOLD
3-WAY VALVE
3-WAY VALVE CLOSED
CARBON COLUMN INFLUENT HEADER VALVE – OPEN
INFLUENT HEADER
WASTE AND DRAIN LINE

FIGURE 5

TYPICAL ARRANGEMENT FOR UPFLOW,
COUNTER CURRENT CARBON CONTACTOR
(FROM CULP & CULP)

more saturated, heavier carbon tends to maintain a position at the bottom of the column where it is withdrawn for regeneration. A semi-countercurrent approach can also be achieved by using two downflow columns in series. As indicated on Figure 6, water is first passed down through Column A, then down through Column B. When the carbon in Column A is exhausted, the carbon in Column B is only partially spent. At this time, all carbon in Column A is removed for regeneration and is replaced with fresh carbon. Column B then becomes the lead column in the series. When the carbon in Column B is spent, the carbon is removed for regeneration and is replaced with fresh carbon. This type of operation gives only some of the advantages of countercurrent operation because only the carbon near the inlet of the lead bed is fully saturated with impurities removed from the water and some capacity is unused in much of the rest of the carbon sent to regeneration. Also, the piping and valving is more complex and costly than for an upflow, countercurrent column. Unless one is attempting to use the carbon for the dual purpose for filtration and adsorption (which the author does not recommend for most cases), there is no advantage to using the downflow approach while there are the disadvantages discussed above. The Technology Transfer Manual, "Process Manual for Carbon Adsorption" (second edition, dated October, 1973) contains several illustrative contactor designs.

The choice of contactor design is also dependent upon the method selected for control of hydrogen sulfide generation in the carbon columns. The hydrogen sulfide is produced by sulfide-reducing bacteria under anaerobic conditions. Conditions promoting or accelerating the production of hydrogen sulfide in carbon contactors include:

- Low concentrations or absence of dissolved oxygen and nitrate in the carbon contactor influent.
- High concentrations of BOD and sulfates.
- Long detention times.
- Low flow-through velocities.

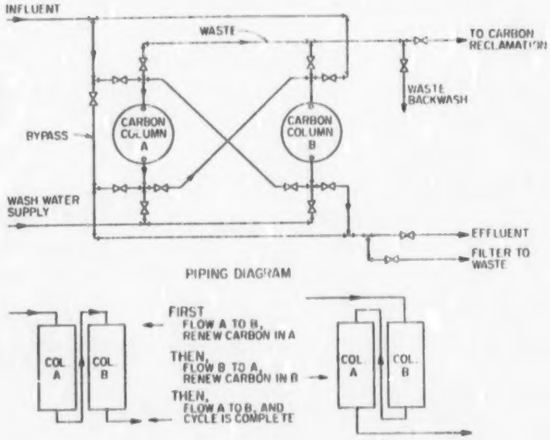

INFLUENT
WASTE
TO CARBON RECLAMATION
WASTE BACKWASH
CARBON COLUMN A
CARBON COLUMN B
BYPASS
WASH WATER SUPPLY
EFFLUENT
FILTER TO WASTE
PIPING DIAGRAM
COL. A
COL. B
FIRST
FLOW A TO B,
RENEW CARBON IN A
THEN,
FLOW B TO A,
RENEW CARBON IN B
THEN,
FLOW A TO B, AND
CYCLE IS COMPLETE
COL. A
COL. B

FIGURE 6

TWO DOWNFLOW CARBON CONTACTORS IN SERIES
(FROM CULP & CULP)

It may be possible to prevent or correct problems of hydrogen sulfide generation by eliminating one or more of the conditions necessary to sustain growth of the sulfate-reducing bacteria. Most of the preventive measures must be provided in the design of the carbon contacting system, but there are also some corrective measures which can be taken in plant operation. The amount of actual plant operation experience in this regard is limited. To provide flexibility for dealing with problems of hydrogen sulfide production in packed beds of carbon, facilities for application of chlorine to the influent should be provided. In addition, in upflow expanded beds it may be desirable to provide for introduction of air, oxygen or sodium nitrate (as a source of oxygen). Because of the mass of cell growth produced, it may be less desirable to introduce air or oxygen ahead of packed beds because of potential physical plugging of the beds. These growths are flushed through expanded upflow beds, but may be removed in sections of the plant which follow such as filters or clarifiers.

Some measures available in the operation of carbon facilities for control of hydrogen sulfide are:

- Columns may be backwashed at more frequent intervals or backwashed more violently by use of air scour or surface wash.
- Detention time may be reduced by taking some carbon contactor units off the line, provided that the reduced carbon contact time is still sufficient to obtain the desired removal of organics and that head losses in the carbon columns remaining on the line do not become excessive.
- Chlorination or oxygen addition may be initiated.

In operations at the PCT pilot research facility at Pomona, California where the carbon influent consisted of chemically clarified raw wastewater, it was found that:

- Continuous chlorination of the carbon column influent at dosages up to 50 mg/l reduced significantly but did not stop H_2S production.
- Intermittent backwash, surface wash and oxygen addition reduced but did not completely eliminate H_2S.
- Intermittent backwash, surface wash and continuous oxygen addition to DO = 4 mg/l reduced sulfide formation but stimulated biological growth and head loss in the carbon bed.
- The addition of air wash to normal backwash and surface wash was not effective against H_2S and 7 inches of carbon was lost from the bed.
- The continuous addition of sodium nitrate to the carbon column influent at the rate of 4 to 5 mg/l as NO_3–N completely inhibited H_2S generation in the column.

At the Cleveland Westerly pilot plant, all efforts to eliminate sufide odors in carbon columns following PCT were found to be impractical. However, the BOD of the carbon column influent at this plant ranged from 80 to 100 mg/l as opposed to around 40 mg/l at Pomona. The control methods used were: (1) daily backwashing at 10 gpm/sq. foot plus surface wash at 2 gpm/sq. foot for 28 minutes, (2) continuous addition of $NaNO_3$ to the influent, and (3) backwashing with water containing 27 mg/l of chlorine (from NaOCl). At dosages of 100 mg/l of $NaNO_3$ (expressed as NO_3) sulfide production was elimated but this high dosage was not considered economically practical.

Sulfides in the carbon column effluent can be removed by precipitation with iron or by addition of chlorine. However, at this time the most effective means of coping with the H_2S problem appears to be to maintain aerobic conditions in the carbon contactors rather than trying to remove H_2S after it is formed. If the BOD applied to the carbon is less than 5 mg/l as is the case in most tertiary treatment schemes, the H_2S problem is easily controlled. For applied BOD values substantially higher than this, it appears that use of upflow, aerobic expanded contactors followed by sedimentation or filtration is preferable.

Also, breakpoint chlorination, prior to downflow beds, although expensive, has been reported effective at Blue Plains in controlling hydrogen sulfide. Since most of the nitrogen can be expected to be on the ammonia form in PCT applications, efficient nitrogen removal could also be achieved with this approach. Higher operating pressures and hence, greater carbon depths may be used in steel pressure contactors. As a result, a concrete contactor generally has a shallower carbon depth and a greater surface area of carbon to maintain the same contact time. Thus, there is substantially more underdrain area and influent and effluent headers per unit of contact time in the gravity concrete structures. Economic comparisons between the two approaches show that there is not a great deal of cost difference in most cases. When using steel contactors, it is imperative that the interior be properly protected from the very corrosive effects of partially dewatered activated carbon. Two 8-mil thick coatings of a coal tar epoxy has proven to be effective at Tahoe over 4 years of continuous operation. Fiberglass-polyester coatings would also be effective although more costly than the coal-tar epoxy coatings. Costs for shop-applied coatings will vary from about $0.50/ft^2 to $2.00/ft^2 depending upon the material and thickness selected. Costs for field applied coatings will be about twice as high. Also, in most cases, the costs for fabricating steel vessels in the field will be substantially higher per pound of steel than for a shop fabricated vessel.

Carbon Regeneration

As granular activated carbon adsorbs organics from wastewater, the carbon pores eventually become saturated and the carbon must be regenerated for reuse. The best way to restore the adsorptive capacity of the carbon is by means of thermal regeneration. By heating the carbon in a low-oxygen steam atmosphere in a multiple-hearth furnace at temperatures of 1,650-1,750 degrees F, the dissolved organics are volatized and released in gaseous form. The regenerated carbon is cooled by water quenching. By proper treatment, carbon can be restored to near virgin adsorptive capacity while limiting burning and attrition losses to 5-10 percent. Regeneration furnace off-gas odors can be controlled by afterburning, if necessary, and particulates and soluble gases can be removed by use of Venturi or jet impingement type scrubbers. Figure 7 illustrates a typical regeneration system.

The carbon furnace should be sized with recognition of the fact that substantial downtime may be required for maintenance of the furnace. An allowance of 40 percent downtime in selecting the furnace size provides a conservative basis for furnace selection. Details on the design and operation of carbon regeneration systems may be found in *Advanced Wastewater Treatment* and in the EPA Technology Transfer Manual, "Process Design Manual for Carbon Adsorption" (second edition, October, 1973).

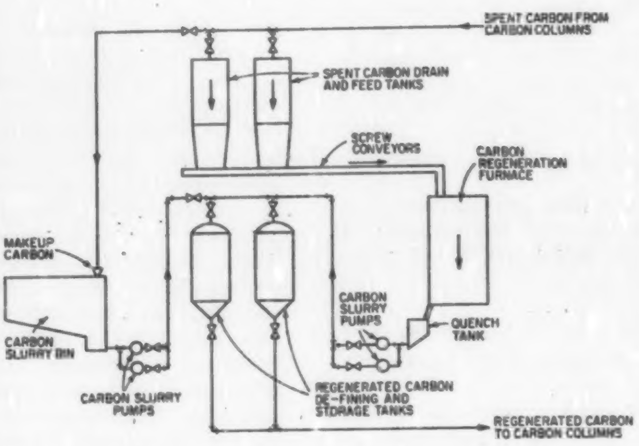

SPENT CARBON FROM CARBON COLUMNS
SPENT CARBON DRAIN AND FEED TANKS
SCREW CONVEYORS
CARBON REGENERATION FURNACE
MAKEUP CARBON
CARBON SLURRY BIN
CARBON SLURRY PUMPS
CARBON SLURRY PUMPS
QUENCH TANK
REGENERATED CARBON DE-FINING AND STORAGE TANKS
REGENERATED CARBON TO CARBON COLUMNS

FIGURE 7

ILLUSTRATIVE CARBON REGENERATION SYSTEM
(FROM CULP & CULP)

ALTERNATE SYSTEMS

Several alternate approaches now being used or investigated for use in various parts of the country are summarized in Figure 8 and some specific cases are described below. The exact effluent quality by each process will depend on the specific influent quality involved; however, the effluent quality achieved in each previous study indicates the general capabilities of each process.

Rocky River, Ohio Study

Rizzo and Schade studied a physical-chemical system for application at Rocky River, Ohio in a 10 mgd plant now under construction. The raw sewage was coagulated with an anionic polymer (about 0.3 mg/l) settled, and then applied to granular carbon columns essentially using the schematic shown in Figure 8-C. The downflow carbon columns serve the dual purpose of adsorption and filtration. In order to provide the phosphorus removal, an inorganic coagulant must be used in conjunction with the polymer. The full-scale plant at Rocky River will use ferric chloride in addition to the polymer to provide phosphorus removal.

Rocky River pilot tests with four small carbon columns in series were performed over a 31-day period. The following table summarizes the results.

TABLE 4

			CARBON CONTACT TIME, MINUTES		
	RAW	CLARIFIER EFFLUENT	14.0	23.4	32.6
Suspended Solids, mg/l	107	65	13	15	7
BOD, mg/l	118	57	21	11	8
COD, mg/l	235	177	67	50	44

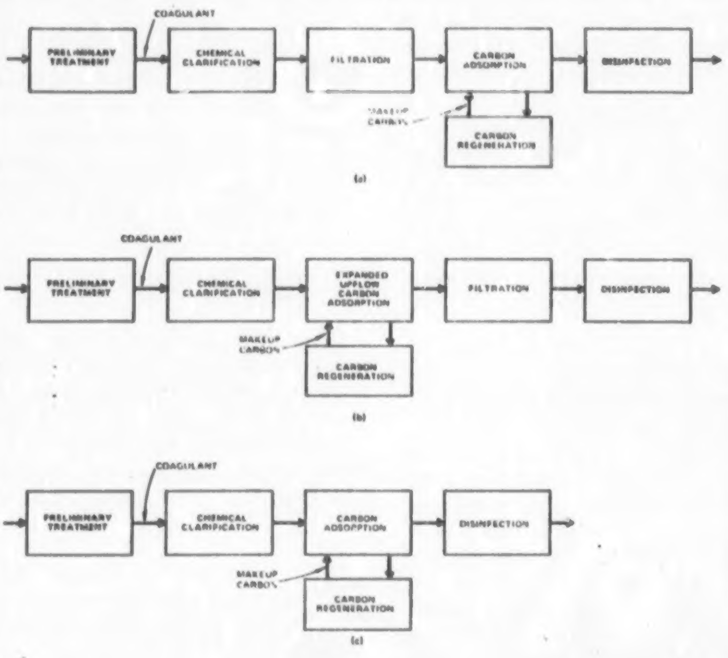

COAGULANT
PRELIMINARY TREATMENT
CHEMICAL CLARIFICATION
FILTRATION
CARBON ADSORPTION
DISINFECTION
MAKEUP CARBON
CARBON REGENERATION
(a)
COAGULANT
PRELIMINARY TREATMENT
CHEMICAL CLARIFICATION
EXPANDED UPFLOW CARBON ADSORPTION
FILTRATION
DISINFECTION
MAKEUP CARBON
CARBON REGENERATION
(b)
COAGULANT
PRELIMINARY TREATMENT
CHEMICAL CLARIFICATION
CARBON ADSORPTION
DISINFECTION
MAKEUP CARBON
CARBON REGENERATION
(c)

FIGURE 8

TYPICAL PHYSICAL-CHEMICAL TREATMENT SCHEMES

Ewing-Lawrence Studies

Weber, et al, have reported on studies conducted at the Ewing-Lawrence Sewerage Authority plant near Trenton, New Jersey. The raw sewage was coagulated, settled, filtered and passed upward through an expanded carbon bed (Figure 8-b). Filtration was also evaluated following the carbon treatment. The degritted raw sewage was coagulated with an inorganic coagulant and then passed through a sedimentation basin at a rate of about 700 gpd/sf. Weber found that there was no significant difference in the adsorption efficiency of a downflow, packed carbon bed and an expanded upflow bed. The expanded beds offered the advantage of not requiring backwash for removal of biological solids. The wastewater used in these studies was very weak as reflected by the primary effluent BOD of 40 to 60 mg/1, with a clarified effluent BOD of only 10 to 20 mg/1 being applied to the carbon. The initial value of soluble BOD is much lower than usually found in municipal wastes. The soluble BOD applied to the carbon stimulated biological growth within the carbon columns. The biological activity is enhanced by the overall capacity for removal of organics by oxidizing a portion of the adsorbed organics. However, the benefit was accompanied by a problem of generation of hydrogen sulfide under the anaerobic conditions encountered in the columns. Addition of hypochlorite to the carbon influent was moderately effective in reducing the hydrogen sulfide odor. Aeration of the carbon influent partially reduced the odor but produced enough biological floc to plug the packed bed adsorbers. The approach finally used was to bleed oxygen into the influent of an expanded, upflow bed whenever there was evidence of hydrogen sulfide in the product water. The 5-day BOD of the carbon effluent averaged 2 to 3 mg/1.

Z-M Process

The basic flowsheet for this process consists of lime coagulation at high pH (11), settling, recarbonation, filtration and granular carbon adsorption. The basic flowsheet of the type shown in Figure 8-a with the requirement of high pH being an integral part of the approach. The process developers claim that the adsorption of the organics found in raw sewage may be improved with the addition of lime to raise the raw sewage pH to a very high value. They feel that this causes hydrolysis of high-molecular-weight organic molecules with resulting lower weight organics being more readily adsorbed. Effluent COD values of 2 mg/1 have been claimed. The pH required to achieve the claimed hydrolysis reaction varies from wastewater to wastewater but is generally in the range of 11.8 and higher.

Biological growths occurred in the carbon columns in laboratory and pilot tests. Carbon contact time was 67 minutes in the pilot plant. The resulting potential H_2S problem was controlled by backwashing the carbon columns whenever the D.O. dropped more than 0.5 mg/1 during the passage through the column. With stronger wastewaters, more typical of municipal wastes, backwashing of the columns based on that D.O. would be impractical. In addition to backwashing on the basis of D.O. decrease, the last portion of the backwash water was chlorinated to minimize biological growth.

During the "best monthly period" of the pilot plant operation, the carbon influent COD of 65 mg/1 was reduced to 2 to 14 mg/1 (average of 8.6 mg/1). During a "stable period" of three weeks, the effluent COD averaged 11 mg/1. The COD of 65 mg/1 applied to the carbon is lower than will be the case for many coagulated and settled raw municipal wastes.

For the Z-M process, large quantities of lime are required to raise the pH to the desired range. Lime requirements of 600 to 800 mg/1 are not unusual. This results in larger quantities of sludge to be handled when compared to the required coagulant dose for good coagulation and phosphorus removal only. Also, the quantities of CO_2 required for pH adjustment are increased. Weber reported on tests in which no benefit resulted from use of the high pH proposed in the Z-M process. Similarly, on-site pilot tests at Cleveland, Ohio which are described below, did not show any benefit from use of a high pH prior to carbon adsorption. Thus, extensive tests should be conducted on any given wastewater to determine if any benefits occurring by raising the pH to these high values offset the additional costs.

Cleveland, Ohio Study

Laboratory investigations and pilot plant studies of physical-chemical treatment of raw sewage at the Westerly plan in Cleveland, Ohio were conducted from July 1970 to April 1971. The study goal was to develop design criteria for a 50 mgd plant now under construction. The basic processes used were coagulation, settling, filtration and granular carbon adsorption(Figure 8-a).

The raw sewage BOD averaged 235 mg/1 and the COD 523 mg/1 during the pilot study. The BOD applied to the carbon averaged about 90 mg/1 and the COD 150 mg/1.

BOD and COD removals averaged 86.5 percent and 92.4 percent, respectively, which correspond to an average effluent BOD of 31 mg/1 and COD of 40 mg/1. Severe problems with generation of hydrogen sulfide in the carbon columns also occurred, and no satisfactory solution was developed during the pilot study.

Blue Plains Study

Physical-chemical treatment of raw wastewater was among the alternates studied by the EPA in their Washington, D.C. pilot plant. The process consisted of lime coagulation, sedimentation, filtration and granular carbon adsorption (Figure 8-a). The raw sewage had an average BOD of 129 mg/1 and a COD of 307 mg/1. Raw sewage was lime coagulated in the pH range of 11.3 to 11.7. About 80 percent BOD removal was achieved by lime coagulation only. Thus, the BOD applied to the carbon was 20-30 mg/1.

Average carbon contact time was 27 minutes in four series columns of downflow, packed bed configuration. Hydrogen sulfide problems could not be controlled by daily backwashing of the lead column. A caustic backwash (600 mg/l NaOH for 30 minutes) of the lead column every other day reduced the biological activity somewhat but H_2S persisted at the 2.5 mg/l level. During early tests, the COD was reduced from 41 to 8 mg/l but later reductions were substantially less, with an effluent COD of 20 mg/1. At a carbon loading of 0.46 pounds per COD per pound of carbon, the carbon from the first two columns was replaced.

Physical-chemical treatment of raw wastewater at Blue Plains (consisting of 2-stage lime precipitation, filtration and carbon adsorption) produced the following average effluent quality over a 10 month period: BOD of 6.2 mg/l (95% removal), COD of 15.5 mg/l (95 percent removal), and 0.13 mg/l total phosphorus (99 percent removal). The H_2S problem was controlled and ammonia removed by breakpoint chlorination ahead of the carbon. Backwashing of the lead column everyday coupled with feeding of 15 mg/l oxygen to the lead column and lesser amounts to each downstream column also controlled the H_2S problem.

FULL SCALE APPLICATIONS

Table 6 summarizes the status of several major projects utilizing physical-chemical treatment of raw wastewaters. The effluent data in Tables 5 and 6 and the author's experience in the evaluation of many wastewaters in the laboratory indicate that the PCT approach is best suited for cases where the effluent BOD requirements are in the 7-20 mg/l range. Most raw wastewaters contain enough non-adsorbable BOD to prevent consistent achievement of BOD values of 1-7 mg/l unless biological treatment precedes carbon adsorption. However, as indicated in Table 6, there are many instances where regulatory requirements fall in the range which can be met by PCT.

SUMMARY

Physical-chemical treatment of raw wastewaters offers performance advantages over biological treatment, in that somewhat higher removals of BOD are generally provided while substantially higher removals of suspended solids and phosphorus are provided. The process is not adversely affected by toxic materials. Substantial savings in space are achieved with physical-chemical treatment. Under some conditions, it may also offer economic advantages.

Not all organics found in municipal wastewaters are adsorbable on carbon. Thus, the limitation on BOD and COD removal will depend on the quantities of these non-adsorbable materials present in a given wastewater. Generally, 90-95 percent BOD and COD removal can be achieved. Techniques are presented which enable the design engineer to evaluate the quantity of nonadsorbable organics present in a given wastewater. Techniques for evaluation of alternate coagulants and the handling of the resulting sludge are also presented.

TABLE 5
SUMMARY OF EFFICIENCY OF PHYSICAL–CHEMICAL TREATMENT OF RAW WASTEWATERS

	INFLUENT* CHARACTERISTICS				EFFLUENT* CHARACTERISTICS			
TEST SITE	BOD	COD	SS	P	BOD	COD	SS	P
Rocky River, Ohio	118	235	107	–	8	44	7	–
Eqing–Lawrence, New Jersey	100	–	–	10	2-3	–	–	1
Z–M Pilot Plant at New Rochelle, N.Y.	–	220	–	7.6	–	2-14	–	0.2
Cleveland, Ohio	235	523	207	5.4	24	50	13	0.5
Blue Plains, D.C.	129	307	–	8.4	6.2	15.5	–	0.13

TABLE 6

PHYSICAL-CHEMICAL TREATMENT PLANTS

SITE	STATUS 1973	DESIGN ENGINEER	AVERAGE PLANT CAPACITY (MGD)	CONTACTOR TYPE	NO. OF CONTACTORS IN SERIES	CONTACT TIME (1) (MIN.)	HYDRAULIC LOADING (GPM/SQ.FT.)	TOTAL CARBON DEPTH (FT.)	CARBON SIZE	EFFLUENT REQUIREMENTS (2) (OXYGEN DEMAND)	FIGURE 8 PROCESS TYPE
1. Cortland, N.Y.	Design	Stearns & Wheler	10	Downflow Pressure	1 or 2	30	4.3	17	8 x 30	TOD < 35 mg/l	C
2. Cleveland Westerly, Ohio	Design	Engineering Science	50	Downflow Pressure	1	26	3.7	17	8 x 30	BOD < 15 mg/l	A
3. Fitchburg, Mass	Construction	Camp Dresser & McKee	15	Downflow Pressure	1	35	3.3	15.6	8 x 30	BOD < 10 mg/l	A[4]
4. Garland, Texas	Design	URS Forrest & Cotton	30[3]	Upflow Downflow	2	30	2.8	10	8 x 30	BOD < 10 mg/l	C
5. LeRoy, New York	Design	Lozier Engineers	1	Downflow Pressure	2	37	7.3	36.8	12 x 40	BOD < 10 mg/l	A
6. Niagara Falls, N.Y.	Design	Camp Dresser & McKee	48	Downflow Gravity	1	30	3.3	9	8 x 30	COD < 113 mg/l	C
7. Owosso, Michigan	Design	Ayres, Lewis Norris & May	6	Upflow Packed	2	38	6.2	30	12 x 40	BOD < 7 mg/l	A
8. Rosemount, Minn	Construction	Banister, Short Elliot, Hendrickson & Associates	0.6	Upflow Downflow Pressure	3 (max.)	66 (max.)	4.2	30 (max.)	12 x 40	BOD < 10 mg/l	—[5]
9. Rocky River, Ohio	Construction	Willard Schade & Associates	10	Downflow Pressure	1	20	4.3	15	8 x 30	BOD < 15 mg/l	C
10. Vallejo, Calif.	Design	Kaiser Engineers	13	Upflow Expanded	1	28	4.8	16	12 x 40	BOD < 25 mg/l (90% of time)	B

(1) Empty bed (superficial) contact time for average plant flow

(2) BOD: Biochemical oxygen demand
COD: Chemical oxygen demand
TOD: Total oxygen demand

(3) 90 mgd capacity

(4) Without filters

(5) Experimental flexibility permits several modes of operation.

Design considerations for the unit processes of coagulation, settling, filtration, carbon adsorption, carbon regeneration and sludge handling are discussed. Design and operational considerations for the control of hydrogen sulfide generations within carbon contactors are also discussed.

Experiences gained at several locales in pilot tests are presented as well as a tabulation of the design criteria being employed in several full-scale installations.

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SYNTHESIS OF CATIONIC POLYELECTROLYTES FOR TREATMENT OF NATURAL AND WASTE WATERS.

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Nowdays reagent treatment of waste waters with the use of highly-molecular organic material-flocculants is one of the most popular methods in practice of natural and waste waters treatment.

Flocculants used together with mineral coagulant or alone afford intensification of water treatment processes, improving its quality, reducing of mineral reagents doses and quantity of formed slime correspondingly, improving of filtering and mechanical characteristics of sludge.

The charge of colloidal particles and flocculant macromolecules is of great significance for adsorption and flocculation.

Coagulation process is facilitated at the expense of electrostatic attraction of contrary charged particles in case if charge of colloidal particles and macromolecules of polymers is different by its sign. The best way to treat natural and waste waters is to use polyelectrolytes with highlybasic ionogenous groups, since the most waste waters pollutants have negative charge.

In connection with this the problem of new cationic polyelectrolytes synthesis and investigation of their physical-chemical properties is of great practical interest.

Besides it must be noted that there is extremely a small number of polymers having high efficiency in processes of water and waste treatment of industrial effluent.

Existing methods of cationic polyelectrolytes synthesis may be directed into two main groups:

- polymersimilar transformation of polymerization and polycondensation linear polymers,
- polymerization of nonlimitive ionogenous monomers.

In the first case cationic polyelectrolytes are received as the result of polymers chemical transformations non-containing ionogenous groups (polystyrene, polyvinyl toluene) or containing lowbasic ionogenous groups (polyvinylpiridine, polyvinylhynoline).

Nonionogenous polymers are chloremethylated and amminated by various tertiary amines: triethylamine, triethanolamine etc. For the purpose of receiving highly basic polyelectrolites at the base of polymers containing lowbasic functional groups, they are treated with different alkylating agents (halogen alkyls, dialkylsulphates etc.).

However given methods of cationic polyelectrolytes synthesis are distinguished by their multistage character, complicating technological scheme of receiving them, by existence of accessory reactions leading to structure formation of polymers and creation of unregular in content polymers. Besides received cationic polyelectrolites, are characterised by comparatively low values of molecular weights.

Therefore one stage process of ionogenous unsaturated monomers polymerization is more perspective as far as it affords receiving highly molecular anionites with maximum ionogenous groups content.

The initial material used for the synthesis of highly basic water-soluble polyelectrolytes were quaternary vinylpyridine salts (QVPS) on vinylpyridine and various alkylating agents base that conditioned by extremely high reactivity of these salts and also availability of source of raw materials.

Monomeric vinylpyridine salts easily enter into polymerization due to high polarization of double connection when positive charge on nitrogen atom. As the double connections are more polarizated in the ortho-and para-positions it is not possible in most cases to receive unlimited quaternary salts on the base of 2 and 4 vinylpyridines because the polymeric products are immediately released in this case.

At the same time as a result of reaction of 2-methyl and 5-vinylpyridines (2M5V) and various alkylating agents the stable quaternary vinylpyridine salts (Q VPS) are formed due to the less activity of the double connection.

It was established that the releasing of poly-I-alkyl-2 methyl -5 - vinylpyridine halides (2 MSV - RX) and poly - I.2 demethyl - 5 - vinylpyridine - n - toluene sulphonates (2 M5V - METSA) is determined by the conditions of carrying out of the reaction: medium polarity, temperature, duration and so on.

A great effect has the nature of alkylating agents (table No I).

Table I

Releasing (weight in p.c.) of QVPS depending on the nature of halide alkyl and radical length.

R	CH_3	C_2H_5	C_3H_7	C_4H_9	C_3H_5
X					
J	80	65	40	15.0	60
Br	78	60	5.0	–	42
Cl	15	–	–	–	

Vinylpyridine salts polymerization was performed by three methods:

- Spontanous QVPS polymerization in concentrated water solutions by specific ion mechanism;
- radical QVPS polymerization in water ethanol solutions;
- radical QVPS polymerization without their intermediate isolation.

QVPS polymerization by three methods affords not only exposing the influence of synthesis method choice on yield and properties of received polyelectrolytes (molecular weight, ionogenous groups concentration etc.), but also comparing efficiency of different synthesis methods for the purpose of receiving polyelectrolytes suitable for natural and waste waters treatment.

Till now general attention of researches was directed at studying of spontanous polymerization of quarternary vinylpyridine salts.

Kabanov discovered that the reaction is going by specific anion mechanism after detailed kinetic investigations of non-limitive quarternary salts at the base of vinylpyridine with dimethylsulphate spontanous polymerization reaction. In result quarternary polymer salts of highly molecular weight are formed and it's significant at their use as flocculants for natural and waste waters treatment.

The fact that reaction is performed without initiators at low temperatures (25-30°C) is highly significant.

Investigations showed that there was rapid fall of polymerization speed at reducing of monomeric salt concentration in solution.

It should be noted that at QVPS concentration 1 mole/1 and lower the reaction doesn't proceed.

Analogical dependence has place for molecular weights of received polymers (drw.I).

The nature of antiions has great influence on spontanous polymerization QVPS speed.

If at 2M5V-METSA salt polymerization for 4 hours yield is 17% of theoretical, at 2M5V-CH_3B salt polymerization yield is 52%; and that is highly probable that it's the result of different nucleophility and mobility of anions, initiating spontanous polymerization reaction.

Total duration of spontanous polymerization reaction in concentrated water solution is floatuating from 24 to 48 hours. Depending on the character of polymerized monomer salt (table 2).

The second method of cationic polyelectrolytes synthesis radical polymerization of QVPS, is distinguished by high productivity (table 2).

It is seen at given data that reaction duration in this case is 6-10 hours.

However, molecular weights characteristic viscosities of synthesized polysalts are significantly lower than those values for polyelectrolites, received by spontanous polymerization. Characteristic peculiarity of quarternary vinylpyridine salts radical polymerization is the influence of media in which the reaction is performed (3). First of all it's conditioned by existence of ionogenous groups and the strength of inter-ionous and inter-molecular interactions of reacting particles and activity of reaction centres depend on the degree of these groups dissotiation.

The speed of 1 - ethyl - 2 - methyl - 5 - vinylpyridine bromide in water-spirit solutions. - increases approximately 4 times at transfer to less ionizing solvent (absolute standard) comparing with the same value in

TABLE 2

Dependence of reaction duration and
polyvinylpyridine salts viscosity.
Characteristics on the way of receiving them.

Salt description	Synthesis method	Reaction duration hr	Polymer yield %	Polymer hund. ml/g
2M5V–C_2H_5Br	Spontanous polymerization.	24	95	8.7
	Radical polymerization	10	93	0.7
	Without isolation of monomer salt.	12	93	0.3
2M5V–C_2H_5J	Spontanous polymerization.	48	91	3.9
	Radical polymerization	8	98	0.6
	Without isolation of monomer salt	12	97	0.24

x) Characteristic viscosity – 0.05 normal solution KBr.

highly polar solvent (water).

QVPS radical polymerization speed depends on monomer salt nature.

So radical length increase at QVPS nitrogen atom from CH_3 to C_3H_7 lead to reducing reaction rate approximately three times.

Table 3 Values of initial rates and total constants of QVPS polymerization in 50% water ethanol solution.

Initiator – asodiisobutyronitrile.

Monomer	Temperature	$V_0 10^4$mole/sec	$K-10^2$
2M5V–CH_3J	70	–	9.84
2M5V–C_2H_5J	70	2.14	5.56
	75	2.96	7.70
2M5V–CH_3Br	75	1.50	3.90
2M5V–C_2H_5Br	75	0.99	2.57
2M5V–C_3H_7Br	75	0.57	1.49

Comparing of iodine and bromine salts polymerization rates constants shows that bromine salts are polymerized slower than iodine salts (table 3). In all probability the difference of kinetic characteristic of these salts is connected with different degree of monomers molecules ionization and growing macroradicals (3).

Water soluble highly basic polyelectrolytes can be received not only by methods of spontanous and radical polymerization of non-limiting QVPS, but also by radical polymerization of the latter ones. without their intermediate isolation.

This one stage method of cationic polyelectrolites synthesis is of interest by two reasons:

Firstly using this method of receiving cationic polyelectrolytes monomer vinylpyridine salts isolation is not required that simplifies the process significantly.

Secondly, this method of polyelectrolytes synthesis is unchangeable in cases when monomer salts are received with low yields or can't be isolated from reaction sphere. For example, monomer salts at the base, of [illegible] -vinylpyridine and different haloid alkyls couldn't be isolated and therefore the last method is the only possible of all above mentioned ways for receiving cationic polyelectrolytes.

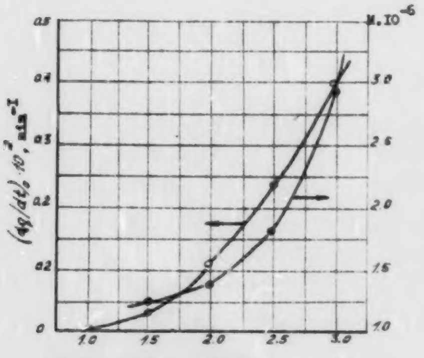
Therefore it should be concluded that all three methods may be used.

The choice of method is defined by definite area and synthesized polymers application conditions.

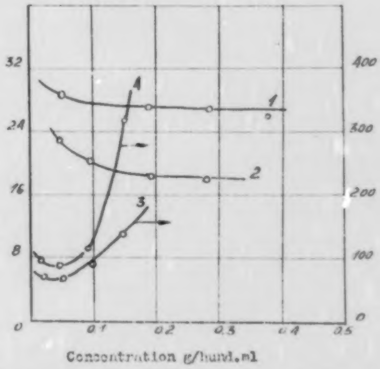
Properties and application of cationic polyelectrolytes at the base of 2-methyl-3-vinylpyridine.

For preliminary appreciation of cationic polyelectrolytes application possibilities as flocculants investigation of their behaviour in water solutions is significant. In particular, investigation of viscous and electrochemical properties of polyelectrolytes solutions reveal the structure condition of polymer macromolecules in solution, its ionogenous abilities, associations of antiions and polyions.

As the result of these investigations it was established that for water solutions of polymer quarternary salts at vinylpyridines base non-linear increase of the viscosity with dilution usual for polyelectrolites is observed. However for polyelectrolites of highly molecular weight received by spontanous polymerization of quarternary vinylpyridine salts viscosity isotherms pass through minimum at definite concentration (C_0) of polyelectrolytes in solution. (drw. 2). At C_0 concentra-



Drawing II. Relation-ship between initial speed of salt polymerization 2M5V - C_2H_5Br and molecular weights of resulting polymerides and initial concentration of monomer. Temperature - 25°C.



Drawing 2. Relationship between reduced viscosity of water solutions of polyelectrolyte HPE-II and concentration at various values of their molecular weights.

[η] hund.ml/g: I - 4.0; 2 - 3.2; 3 - 6.0; 4 - 8.3;

tion the increase of the viscosity is observed, which is explained by aggregation of macromolecules at the expence of intermolecular interactions.

Studying of electroconductivity of polymer and monomer vinylpyridine salts shows their significant difference.

Firstly, equivalent electroconductivity of polymer salts is lower than manomers (table 4). Secondly, isotherms of electroconductivity for polymers have curvilinear concave character.

Table 4

Equivalent electroconductivity of water solutions of QVPS and polyelectrolites at their base at concentration 0.015 mole/l.

Description		Equivalent electrical conduction		hund. ml/g
polyelectrolite	Monomeric salt	monomer	polymer	
HPS-I	2M5V-METSA	49	16	2.0
HPS-6	2M5V-CH_3J	88.5	17.9	1.0
HPS-7	2M5V-C_2H_5J	83.5	15.2	1.2
HPS-8	2M5V-C_3H_7J	80.5	12.85	0.9
HPS-10	2M5V-CH_3Br	92.0	30.6	3.2
HPS-11	2M5V-C_2H_5Br	85.0	36.5	4.0

These features of electrochemical properties of solutions are conditioned by series of specific characteristics distinctive only for polyelectrolytes (counterion connection, association of ions). Values of seeming constant ionization calculated with the help of Kachalcky-Spitnik equation have extremely high values with the range 3.9-4.85 indicative of presence of counterion association in polyelectrolytes water solutions.

Investigations associated with the treatment of natural and waste water with utilization of synthesized polyelectrolytes showed their high efficiency.

So the investigation of flocculating capability of polimeric halogen containing vinylpyridine salts for removing of humus substances from natural water was carried out together with Voronezh State University of Lenin's Komsomol.

The investigations were carried out with water solutions of humic acid and fulvic acid with 2-10 mg/L concentration. The concentration of ionogenous groups of fulvic acids was 5.57 mg.equiv/g. The content of carboxylic groups and the summery concentration of carboxylic and fenolic groups of humic acids are turned out to be 1.41 mg.equiv/g and 3.52 mg.equiv/g. HPS-6, HPS-7; HPS-II were used in salt and OH-form as the flocculants. The conversion into the OH-form is accompanied by yield of weakly basic groups in polyelectrolytes.

It is determined by isomerization of hydroxide alkyl vinylpyridine formed when changing the gallogen-ions to OH-groups; as a result the methylene bases containing tertiary amino groups are formed.

Exchange volume of polyelectrolite found according to the highly basic groups and the summary of highly and weakly basic groups is given in Table 5.

The flocculants volume determined on the basis of data of potentiometric titration.

Table 5

The flocculants volume determined on the basis of data of potentiometric titration.

Flocculant description	Volume mg. eqiv./g	
	acc. to highly basic groups E_I	acc; to summary of highly and weakly basic groups E_2
HPS-6	2.41	4.27
HPS-7	3.45	4.32
HPS-II	3.45	5.50

The presence of acid groups in humus substances and general functional groups in flocculants permit to suppose that the yield of humic acid and fulvic acid is occured at the expense of chemical interaction of these groups. In this case the polymer consumption should be calculated according to the formula:

$$G = \frac{E_{HA}}{E_F} \cdot C$$

$$G = \frac{E_{FA}}{E_F} \cdot C$$

G - polyelectrolite dose, mg/L

C - concentration of humic and fulvic acids in the water, mg

E_F ; E_{FA} ; E_{HA} - exchange volumes of the flocculant; fulvic acid and humic acid, mg. equiv./g.

However, the designed doses for polyelectrolites in OH – form extremely exceed the experimentally-found doses of flocculants. (table 6).

It points to the fact that the flocculation process is determined not only by the volume of humus substances and polybasic but the size of molecule of these compounds.

Table 6
Designed and experimentally-definite doses of flocculants.

Flocculant description	Designed doses of flocculants mg/mg						Experimental doses of acids mg/mg	
	E_{IF}			E_{2F}				
	E_{IHA}	E_{2HA}	E_{FA}	E_{IHA}	E_{2HA}	E_{FA}	humic acid	fulvic acid
HPS-6	0.59	1.46	2.30	0.31	0.82	1.30	0.8-0.9	0.6-0.7
HPS-7	0.41	1.02	1.62	0.32	0.81	1.25	0.9-1.0	0.6-0.7
HPS-II	0.42	1.06	1.70	0.25	0.64	1.1	0.6-1.2	0.6-0.7

As it was established the cationic polyelectrolites on the basis of vinylpyridines may be used successfully for industry waste water treatment. But highly molecular polyvinylpyridine salts obtained with the help of spontaneous polymeryzation of QVPS are the most efficient flocculants.

So the utilization of HPS-II flocculant with 700000 molecular weight permit the treatment of waste water containing acid dyes, petroleum products, dissolved and emulsificated organic substances for 95-100%. The results of using of synthesized polyelectrolytes for industrial wastes treatment are given in the report "Investigation of the waste water treatment with flocculant utilization" made by I.N. Myasnikov; L.V. Gandurina; and L.N. Butseva.

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Physical - Chemical Treatment of Wastewaters from the petroleum Refining - Petrochemical Industry*

by
William J. Lacy and Allen Cywin**

Introduction

Let us define wastes, for the moment, as misplaced resources of human industry. I say momentarily because all wastes have use in some time frame and in some ecosystem. The time frame is impacted by technology and need. time, need, place, and technology then, all determine the scope of industrial wastes problems. Yesterday's moldy bread is today's penicillin. Last month's paper mill wastes could be tomorrow's road binding materials, cooking sauces, medicinals, or activated carbon. Pollutants may, therefore, be considered as the wrong substances in the wrong places at the wrong time.

Industrial wastes are principal point sources of controllable waterborne wastes. In terms of the generally quoted measurements of BOD_5 for strength and volume, the gross wastes of manufacturing establishments are about three times greater than those of the U.S. sewered population. Moreover, the rate of U.S. industrial production, which gives rise to industrial wastes, is increasing at about 4.5 percent per year or over four times faster than the population growth rate. Add to this the extensive variations of composition of industrial wastes, and one realizes that the solution to industrial water pollution is of paramount importance in the environmental protection effort.

Some large refining and petrochemical plants in the United States treat their wastes economically. However, the use of the same technology may not be economical for the treatment of wastes produced in similar but smaller plants.

At present, some 34 refineries discharge their wastes to the community sewer system and depend upon the municipal sewage plant for the treatment. However, most refineries do not have sewer systems readily available and thus must provide their own treatment facilities. It thus becomes important that more economical methods for the treatment of control of wastes be developed by industry. Ideally, a process for treating wastes from an industry should:

1. Effect the removal of the pollutant at minimum cost.
2. Provide for the economical recovery of any valuable by- or co-products.
3. Comprise a technique that would permit the recycling of recovered materials, including water, back to the production operation.
4. Be simple and require minimum operating labor.
5. Require relatively low capital investment.

Reduction of industrial waste discharges is often accomplished efficiently and economically by process modivications, improved housekeeping, and reuse-recycle water management practices. During the period 1954-1968, total water use by all U.S. industries increased 70 percent, but water intake only increased 34 percent. All U.S. industries achieved a reuse ratio 2.30 in 1968. The plants with the 20 best recycling rates in 1970 have very high recycling rates because of low raw water dissolved solids, low ambient air temperatures, and use of high temperature cooling, all of which permit higher recycle ratio (2). By contrast, the Organic Chemicals Industry (which includes the petrochemical industry and is categorized herein by SIC 2815: Cyclic Organic Chemicals) had a reuse ratio of 1.90 in 1968, a net decrease of 4 percent over that of 1964 census. Although the total water usage increased only 20 percent, water intake increased 25 percent, indicating an ineffective utilization by this industry of potential recycled water and/or multiple use of water. In comparison, petroleum refining has achieved an average reuse ratio of 5.25 in 1968, an increase of 63 percent since 1954.

In 1970, industry produced 15.3 trillion gallons of wastewater, compared to 5.3 trillion gallons for the sewered population of the U.S. (3). The industry process water use only was equivalent to 63 percent of all domestic consumption (4). It would appear that extensive wastewater reuse by industry should, therefore, have a substantial impact on water conservation in the U.S. This is of particular significance now in water shortage areas and, in the future, in water-abundant areas.

Although water reuse has remained essentially constant during 1964-1968 for the Organic Chemicals Industry, absolute and substantial increases in the reuse ratio are potentially possible under appropriate circumstances. Past occurences of water reuse have been motivated by the pressures of limited water supply, poor water quality, and more recently, environmental considerations. The latter, particularly in view of existing legislation, should accelerate the trend in the near future.

Gross water demand projections for the next 50 years were made on the basis of industry growth projections and on the assumption that the goal of "no pollution discharge" is achievable by the year 1985 (Table 1).

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* Presentation of the Joint US-USSR meeting on P–C treatment, Cincinnati, Ohio November 1975.

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TABLE 1
GROSS WATER DEMAND PROJECTIONS

	Gross Water Demand	Consumption	Intake	Discharge
	(Billion gallons per day)			
1970	11.6	0.42	4.20	4.8
1985	23.2	0.84	0.84	0
2000	35.8	1.30	1.30	0
2020	72.4	2.62	2.62	0

It is obvious that after achieving closed loop systems by 1985 that the volume of intake required approaches being equal to consumption.

After 1985, intake rates are expected to increase in direct relation with industrial production and gross water demand.

Now, let us speak more explicitly of the petrochemical and petroleum refining industries. The major sources of pollution in these industries may be delineated as shown (5):

1. Crude oil processing: distillation; desalting
2. Cracking Processes: catalytic and thermal; coking
3. Hydrotreating
4. Petrochemical operations
5. Lube oil manufacturing
6. Boiler and cooling tower blowdowns
7. Sour water stripping
8. Contaminated storm runoff
9. Intake water treatment
10. Storage and transfer
11. Leaks and spills

Such wastewaters may contain various salts, acids and alkalies, ammonia, sulfides, solids, and mixtures of organics of varying biodegradability, phenols and other taste- and odor-producing chemicals, and heavy and light oils. Furthermore, wastewaters so generated typically exhibit a BOD and COD range of 100 to 10,000 mg/l and 200 to 15,000 mg/l, respectively, with an average of 1,150 mg/l BOD and 3,100 mg/l COD (6), (7), which is

TABLE 2. TYPICAL REFINERY AND PETROCHEMICAL WASTEWATER CHARACTERISTICS (7) (8) (9)

Petrochemical Principal Products	Waste Flow mgd	BOD mg/l	COD mg/l	SS mg/l
Phenol, Ethylene	2.0	300	1,200	300
Acrylonitrile	0.302	–	1,200	239
Fatty Acids, Esters, Glycerol	0.10	10,000	14,000	–
Azo & Anthraquinone dyes	0.94	352	1,760	152
Ethylene, Alcohols, Phenol	5.9	1,700	3,600	610
Acrylonitrile, Acetonitrile, Hydrogen Cyanide	3.9	390	830	106
Butadiene, Alkalate, MEK, Styrene, Maleic Anhydride	2.0	1,870	–	10
Butadiene, Maleic Acid, Fumaric Acid, Tetrahydrophthalic Anhydride	3.605	959	1,525	–
Phenols	0.215	6,600	13,200	–
Acids, Formaldehyde, Acetone, Methanol, Ketones, Nitric Acid, Nylon Salt, Vinyl Acetate, Actaldehyde	3.46	530	10,130	160
Isocyanates, Polyols, Urethane Foam	0.57	421	1,200	50
Acetaldehyde	1.15	20,000	50,000	200
Ethylene, Propylene, Butadiene, Alpha Olefins, Polyethylenes	0.750	155	380	120
Butylene Isomers, Butadiene, Maleic Anhydride, Fumaric Acid, Tetrahydrophthalic Anhydride, Alkalate, Aldehydes, Alcohol	1.50	1,960	2,980	–
Refinery – Class A	.22	20	120	40
Refinery – Class B	.99	250	750	180
Refinery – Class C	2.98	300	1,080	240
Refinery – Class D	4.35	160	510	130
Refinery – Class E	7.93	200	520	90

indicative of the strength of the wastewaters. In Table 2 are listed some typical wastewater characteristics resulting from these industries.

The treatment of wastewaters from refineries and organic chemicals manufacture becomes apparent with evaluation of the nature of waste to be treated – that of its relative biodegradability and normally higher strength. Figure 1 is an empirical diagrammatic representation of the biodegradability of wastes encountered in this portion of petrochemical industry. Organics in general and petrochemicals in particular may be characterized typically as to their respective abilities to degrade biochemically: Type (a) classical log growth curve, similar to domestic waste; Type (b) requiring a longer lag or retention time for the enzymatic systems of the micro-organisms to become more fully developed – a semi-biodegradable waste; Type (c) a long period of "seed" acclimation required before assimilation of organics proceeds – a semi-refractory waste; and Type (d) essentially no biochemical action due to a refractory waste. Petrochemical wastewaters generally fall into the range of a type (b)-Type (c) waste as depicted by the cross-hatched area in the figure. Several explanations have been postulated for this anomalous behavior (11): (a) reaction rates of individual components (organics) may differ markedly, (b) the bio-mass present may not utilize some of the constituents due to the absence of the proper enzymes (catabolic and biosynthetic enzymes and permeases must all be present in proper concentrations), and (c) there may exist materials causing inhibition or repression (interference in the natural metabolic pathway). An additional factor that must be taken into account, and one that may be the most significant, is the formation of intermediates and end-products of metabolic pathways that diffuse out of or are released by cell lysis. These products may exhibit a profound effect on the biodegradability of the waste. Extracellular quantities of these intermediates and metabolites often are indistinguishable from the original waste components, and due to the non-specificity of either the BOD or COD analysis, such a change in concentration cannot be monitored directly and "a waste which is biodegradable may appear to be 'hard' because of the intermediates which have passed into the medium during the given detention time" (11, p. R488). Table 3 contains a list of 24 organic compounds found to be biorefractory (12). Similar compounds have been identified in the municipal raw water intakes (Mississippi River and tributaries) and/or finished water supplies at or near New Orleans, Louisiana (13). Therefore, it is apparent from the previous discussion that petrochemical and refinery waste treatment practices present the environmental/chemical design engineer with a formidable challenge including what physical-chemical treatment process to utilize.

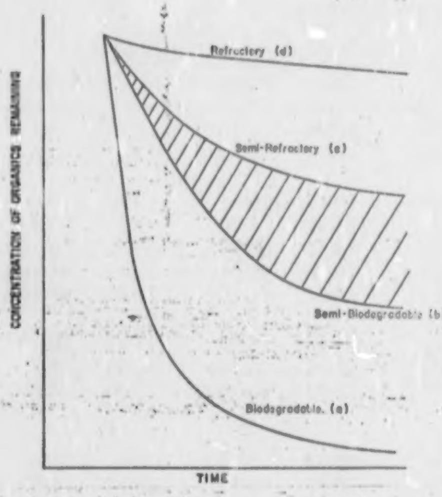

FIGURE 1 – TYPES OF PETROCHEMICAL WASTEWATER AND THEIR RELATIVE BIODEGRADABILITY (10)

TABLE 3. REFRACTORY INDUSTRIAL WASTES (12).

*nitrobenzene
trichloroethane
tetrachloroethylene
chloroethyl ether
chloromethyl ethyl ether
chloropyridine
chloronitrobenzene
dichloroethyl ether
*benzene
*toluene
camphor
veratrole (1, 2-dimethoxy benzene)
guaiacol (methoxy phenol)
borneol (bornyl alcohol)
isoborneol
*ethylene dichloride
chlorobenzene

bromobenzene
dichlorobenzene
bromochlorobenzene
*ethylbenzene
chloroform
*styrene
isopropylbenzene
butylbenzene
dibromobenzene
*isocyanic acid
*methylchloride
bromophenylphenyl ether
*dinitrotoluene
methylbiphenyl
acetone
2-ethylhexanol
2-benzothiozole

*These compounds also have been found to impart taste and odor to drinking water supplies in trace amounts (13).

There are indications that industry is well aware of the benefits of recyling cooling tower blowdowns (14). One such example concerns a Class "E" refinery where "the cooling towers are used to reduce the concentration of organics and to concentrate the undesirable precipitates. Thus, all wastewaters originating from plant operations and storm water runoff are either recycles into the process streams and reused or recycled in the cooling towers" (15,p. 242). If wastewater reuse is developed and implemented to its maximum potential, it could provide industry with a viable technique for pollution control, which could conceivably be the least expensive alternative for fulfilling future regulatory requirements. In fact, if no discharges of wastewater are achievable and practicable, the need to obtain a permit

TABLE 4 NET RAW WASTE LOADS FROM PETROLEUM REFINING INDUSTRY CATEGORIES (50 Percent Probability of Occurrence)

KILOGRAMS/1000 M^3 (LB/1000 BBLS)

SUBCATEGORY	BOD5	OIL/GREASE	PHENOL	AMMONIA
TOPPING	3.43(1.2)	8.29(2.9)	0.034(0.012)	1.20(0.42)
CRACKING	72.93(25.5)	31.17(10.9)	4.00(1.4)	28.31(9.9)
PETROCHEMICAL	171.6(60)	52.91(18.5)	7.72(2.7)	34.32(12)
LUBE	217(76)	120.1(42)	8.3(2.9)	24.1(8.5)
INTEGRATED	197(69)	75(26)	3.8(1.3)	20.5(7.2)

to discharge effluents would be precluded. Add to this the water conservation aspect and the potential savings resulting from reduced effluent monitoring, and the total recycle concept has even greater appeal.

As shown in Table 4 the largest percentage of the waste load entering our waterways is derived from the more complex types of refinery operations. It should be evident that more than half of each of the five important water pollution loads originate from Class D to E refineries.

The data presented in Table 5 show that Class D and E refineries account for about one third of U.S. refining capacity. It is, therefore, evident that, generally speaking, unit waste loading per barrel of crude processed increases with increasing refinery complexity. This would indicate the need for higher efficiency pollution control systems for the more complex refinery as necessary, should it be desired to achieve the same water discharge load per unit of capacity as for less complex refineries. This data also indicate that the more complex refineries have larger capacities and are the larger point sources of waste loads.

TABLE 5. DISTRIBUTION OF REFINING CAPACITY BY REFINERY COMPLEXITY (9)

Refinery Classification	Number of Refineries	Capacity MBCPD	% of Total U.S. Crude Capacity
A	13	13	2
B	72	46	25
C	27	116	25
D	11	92	8
E	13	227	24

Table 6 shows treatment control efficiencies possible with use of applicable technologies such as biological systems and activated carbon adsorption, as compared to the overall industry average being achieved at this time. It illustrates that substantial improvements to pollution control may be attained by the refining industry by application of either well-demonstrated technology (biological systems) or newer and emerging physical-chemical technology such as activated carbon adsorption.

TABLE 6 Typical Removal Efficiencies for Oil Refinery Treatment Processes

	PROCESS	REMOVAL EFFICIENCY							
	INFLUENT	BOD_5	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE
API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA
Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA
Dissolved Air Flotation	1	20-70	10-60	NA	50-85	10-85	10-75	NA	NA
Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA
Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100
Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100
Activative Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100
Tpickling Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100
Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA
Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA
Filter									
Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA
Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA

Data Not Available

In addition to wastewater treatment technology, refineries also have pollution control concerns with process sludges, waste chemicals and thermal discharges in the form of cooling water. The question of toxic, hazardous, and/or taste and odor constituents in refinery discharges of any sort must also be faced.

WATER POLLUTION CONTROL TECHNOLOGY

Table 7 illustrates the technological areas that are, in general, pertinent to effective pollution control for the Organic Chemicals and Petroleum Refining Industries. The specific solutions available to each plant will be determined by several factors–and economics (overall economics) will oftentimes be the most important of these. By and large, one must recognize the need to detoxify and/or degrade toxic wastes, control discharges of nutrients and salts (possibly through by-product recovery techniques), and reduce or eliminate inadvertent high strength wastewater releases to quantities that produce little or no ecological effects on receiving streams. Where the receiving waters are too sensitive to any permissible waste discharge, the development and implementation of "no discharge" systems of pollution control may be required as the means to meet local or national environmental standards (presently and in the future).

Physical and chemical and lower cost methods of control will, of necessity, continue to be developed and demonstrated. Improving performance and upgrading existing treatment technology in conjunction with supplemental advanced wastewater treatment physico-chemical add-on processes (i.e., tertiary treatment) may be necessary, particularly for special side streams difficult to treat by biological methods, as well as alternative methods for implementation by both old and new facilities. Sludges and chemical wastes, specific pollutants, (e.g., halogenated hydrocarbons, heavy and toxic metals, etc.,) and comprehensive water pollution control methods, including regionalization, also must be further

TABLE 7. POLLUTION CONTROL TECHNOLOGY STATUS IN THE PETROCHEMICAL AND PETROLEUM REFINING INDUSTRIES.

Technology	NEED FOR			Applications & Objectives
	Research	Development	Demonstration	
Biological oxidation	some	some	yes	(1) Multi-stage biox systems (2) To achieve and maintain 90-95% BOD removal for single stage systems. (3) Need pre- and post-treatment process/operations to improve performance and reliability of both single- and multi-stage Biox.
Sludge disposal	yes	yes	yes	(1) Solids disposal: a) Land assimilation b) Incineration (fuel value) c) Catalylic oxidation d) Solvent extraction e) Wet oxidation and pyrolysis
Advanced treatment	yes	yes	yes	(1) Biox alternatives (2) To achieve and maintain 95-99% pollutant reductions (3) By- and co-product recovery (4) Refractory organic removal (5) Biox supplement
Closed loop systems	yes	yes	yes	(1) No discharge (closed cycled systems) (2) Cost of water (3) Water conservation and resue (4) Containment of trace toxic chemicals
Comprehensive approach	–	yes	yes	(1) Total environmental effects (2) Basin planning (3) Joint treatment (4) Synergistic benefits

developed and improved.

As a result of the EPA perspective of the state-of-the-art, the Industrial Pollution Control program developed to date in the Petroleum Refining and Organic Chemicals Industries is depicted in Table 8. In recent years, a total of 29 grants/contracts have been awarded covering RD&D projects concerned with wastewater characterization and treatment costs, base level of treatment (biox), advanced waste treatment applications, and recovery (by-product and recycle/reuse) techniques. EPA support amounted to $5,428,700 or 47 percent of total estimated project costs of $11,481,600.

One recently completed development project (Project No. 12020 EEQ) resulted in the successful operation of a completely mixed activated sludge process for treatment of a propylene glycol process wastewater. This wastewater was characterized by a high salt content (9-10 percent NaCl), a pH of 11-12, relatively high concentrations of the glycol (500-1,000 mg/l), together with small quantities of related reaction products (in concentrations amounting to less than 100 gm/l), namely, the oxide, the dichloride, the chlorohydrin, the

TABLE 8. EPA RDGD GRANTS FOR POLLUTION CONTROL IN THE PETROLEUM REFINING AND ORGANIC CHEMICALS INDUSTRIES

Grantee	Total Cost ($1,000)	EPA Grant ($1,000)	Primary Effort			Technological Objectives
			R	DV	DM	
C. W. Rice**	56.3	56.3	X			Treatment costs-general
Engineering Science**	11.2	11.2	X			Wastewater characteristics
Engineering Science**	17.0	17.0	X			State of the Art
E.I. du Pont	874.5	150.1	X			Ocean dispersal of salt waste
State of Louisiana	69.0	48.3	X			Recovery: Membrane systems
MCA	60.0	42.0	X			Effects of Cl_2 on treated organics
Union Carbide	67.1	46.9	X	X		*Biox: Anaerobic inhibitors
State of Louisiana	67.3	32.5	X			Concentration of wastes by dialysis
Datagraphics**	6.7	6.7	X			Treatment costs-organics
Univ. of California	86.7	81.2	X			Recovery: Volatile solvent extraction of organics
Texas A&M Univ.	38.5	34.9	X			Recovery: Solvent extraction
Univ. of Missouri	38.5	36.4	X			AWT: Carbon sorption & regeneration
Ga. Tech.	76.1	71.4	X			AWT: Radiation treatment of high strength chlorocarbon wastes
Union Carbide	314.9	220.4		X	X	*Biox: Refractory organic wastes
Dow Chemical	282.5	197.7		X		Biox: Polyhydric/saline wastes
Celanese	600.0	395.3		X		Biox: Chloraldehyde wastes
Dow Chemical	226.6	142.3		X		Biox: Optimization thru automation
State of Louisiana	827.6	457.8	X	X		AWT: Refractory chlorocarbon wastes
Dow Chemical	196.4	108.3		X		AWT: UV Cl_2 of organic acids in waste brines
Delaware R.B.C.	995.7	646.7		X		AWT: Joint industrial/municipal wastes
Union Carbide	554.1	231.8		X		Recovery: Cooling water blowdowns
B. F. Goodrich	823.1	364.9			X	Biox: PVC wastes
Dow Chemical	1300.4	509.8			X	AWT: Phenol/Acetic acid waste brines
State of Alabama	989.5	314.5			X	Deep well disposal of wastes
CIBA – Geigy	1268.3	392.6			X	*Biox: Plastic media trickling filters
General Tire & Rubber	938.7	461.9			X	Recovery: Distillation for renovation
International Ozone Inst.	15.0	8.0	X			AWT: Ozone
Dow Chemical	181.1	110.0	X	X		Zero discharge: R.O.–Electrodialysis
Union Carbide	498.8	231.8		X	X	Zero discharge: voided processes
TOTAL	11481.6	5428.7				

**Contract *Multi-stage systems

chlorinated ether, and some acetol and acetic acid. A unique mixed culture, which tolerates high salt content and utilizes glycols as the only carbon source, was developed; however, an acclimation period of 6 to 8 weeks was required. TOD removal efficiencies of over 90 percent were obtained at retention times of 8.0 to 9.0 hours and loadings of 2.0 to 3.0 lbs TOD/lb MLVSS-day. Based upon such favorable results and the demonstration of the consistent reliability of the TOD and TOC parameters for correct interpretation of the behavior and fate of the organics in the wastewaters and for the evaluation of the treatment process, a subsequent grant was awarded (Project No. 800766) to develop control systems such that an activated sludge process could be operated as efficiently as a chemical process on a continuous basis; the premise being that the performance of an activated sludge process can be further improved and its reliability increased under steady state conditions. Such conditions can only be achieved by instrumentation to control: (a) the food to microorganism ratio in the aeration vessel; (b) the nitrogen and phosphorus requirements; and (c) the biomass/organics reaction temperature. An additional requirement included the development of a dependable biological toxic detector to sense and eliminate (through proper feed forward and feed backward controls, the influent wastewater may be temporarily diverted to a holding basin) a toxic substance prior to its entry into the aeration basin.

More recently, efforts are being directed toward the development and evaluation of improved physicochemical techniques, both for pretreatment, special segregated side streams, and tertiary treatment supplementation for, or as alternatives to, biological systems. Also, the emphasis continues to be placed upon closed-loop water reuse technology and by-product recovery. There exists today in an area of southwestern Puerto Rico, a large integrated refinery/petrochemical complex, including an electrical generating facility. The cumulative wastewater discharge exceeds 400 MGD (cooling, process, and boiler feed blowdowns) which includes excess heat, organic matter, suspended solids, total nitrogen and ammonia, oil and grease, and phenol. The petrochemical complex produces 775 million #/yr of ethylene and derivative products, including butadiene, ethylene oxide, phenol, cumene, polyethylene, bis phenol-A, plasticizers, refined ethylene and diethylene glycols, ethyl-hexanol, istobutanol, and butanol (23) (24); whereas the integrated refinery processes approximately 175,000 bbls/day of crudes for the production of aviation and motor gasoline, jet fuel, kerosene, disel cyclohexane, isobutanol, propylene, and ethylene(23). It should be noted that a large percentage of the total wastewater flow is cooling water. A grant (Project No. 801398) for a water reuse project has been awarded by EPA. The demonstration phase of the proposed study, which entails the utilization of an optimized AWT system that will deliver treated water for use in heat transfer systems, will be conducted at Ponce, Puerto Rico. One of the major objectives of this project will be to provide quality criteria for water usage in the petro-chemical industry, including quality criteria that

TABLE 8.

Grantee	Total Est. Cost ($1000)	EPA Grant ($1000)	Primary Effort R&D	Demo	Technology
Univ. of Okla.	18	14	yes		State of the Art
Texas A&M	234	40	yes		Catalyzed Oxidation of Phenol and Amines
Harvard	16	15	yes		Pretreatment for Biox (Oil removal)
Illinois Tech	12	35	yes		Pretreatment for Biox (Oil removal)
API	85	51	yes	Pilot Plant	Improved Biox Assimulation of oil
A-D-M Co.	245	107	yes	yes	Pretreatment for Biox (Oil removal)
American Oil	355	170	yes	yes	Oily Sludge and Chemicals Disposal (fluid bed incineration)
Shell Oil	100	70	–	yes	Oily sludge disposal (soil cultivation)
American Oil	1738	337		yes	Post-treatment for Biox (chem coag, dissolved air flotation)
American Oil	226	74		yes	Post-treatment for Biox (mixed media filtration)
Atlantic-Richfield Oil	1160	275		yes	Advanced treatment (Activated carbon with joint treatment alternate)
BP Oil	2625	350	yes on water reuse	yes	Advanced treatment (Rapid Sand Filtration with Activated Carbon)
TOTALS	6844	1538			

are limiting factors with respect to reuse of renovated wastewaters, namely boiler-ffed water, cooling water, service water, and process water. The successful completion of this project will have immediate and obvious impact on the environment of south central and western Puerto Rico, and it is anticipated that the results should show that a significant step can be achieved toward total recycle and reuse of petrochemical wastewaters.

In a recent grant with the Dow Chemical Company (Project No. 803085) the problem of zero discharge from petrochemical plants is being studied. This project will focus on the removal of refractory organic contaminants and the recovery of industrially reusable brines by a reverse osmosiselectrodialysis process. The proposed use of these brines is in the production chlorine which can be utilized for production back in the plant. If successful, this project will evaluate the total reuse of petrochemical wastewaters.

The main objective of total water pollution control within an Organic Chemicals Industrial complex is based on the concept that water pollution abatement and water conservation are economically compatible, particularly for the long term. As water availability becomes more critical, the reuse of water will be dictated by economics, with attendant inherent treatment costs merely a normal operating expense.

A Los Angeles area refinery impounds the periodic storm flow, treats it by contact with granular activated carbon, and then discharges it into a local channel. Because of the highly seasonal nature of the rainfall, it is essential that the treatment system be able to start up and shut down without delay or difficulty. Of course, this eliminated any possibility for the use of biological systems. The operation of this plant demonstrated the reliability, economics, and efficiency of activated carbon treatment of wastewaters on an intermittent basis.

At another refinery, the full scale activated carbon plant was not performing as well as had been expected. The addition of a Bio-Disk pilot plant prior to the carbon columns greatly improved the effluent quality. This follows logically, since the hydrocarbons that are not removable by activated carbon (polar molecules) are highly biodegradable. The reverse is also true, those materials that are refractory usually show amenability to carbon removal.

In another recently completed grant (12050 EZG)), the disposal of oily sludges from petroleum refineries by land spreading was evaluated. Some micro-organisms normally present in soil will attack petroleum hydrocarbons and utilize them as their sole source of carbon. Poorly aerated soils become anaerobic, and under these conditions, the micro-organisms decompose oily material very slowly. Aeration of soil by frequent cultivation is a means of supplying oxygen essential for the more rapid acting aerobic microbes. Temperature, moisture, soil properties, oily sludge properties, and nutrient content all influence the rate at which the hydrocarbons are decomposed.

According to an EPA national analysis of the industry, the attainable concentrations from the application of best practicable control technology currently available are shown on table 9.

Table 9

Attainable Concentrations from the Application of
Best Practicable Control Technology Currently Available

Parameter	Concentration mg/l
BOD_5	15
COD	80-115
TOC	(2.2 X BOD_5)
SS	10
O & G	5
Phenol	0.1
NH3–N	2–10
Sulfide	0.1
CrT	.25
Cr6	.005

CONCLUSION

The Research, Development, and Demonstration grants program of EPA has been implemented to meet current and emerging needs for water pollution control and energy conservation in the Petroleum Refining and Organic Chemicals Industries.

Since the trend toward industrial water reuse has already commenced (e.g., the Petroleum Refining Industry), the exception ocurring in some areas of the Organic Chemicals Industry, acceleration of the trend would provide a sound basis for future industrial expansion. Since current and future environmental standards are expected to increase greatly the pressures to reduce dramatically, or eliminate altogether, pollutional loads and effluent discharges, reuse and recycle to the point of providing an industrial closed water cycle should be planned. On this point, Federal legislation calls for the elimination of the discharge of pollutants into navigable waters by 1985, as a goal.

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EXAMINATION OF OIL-CONTAINING WASTE WATERS CHEMICAL COMPOSITION AFTER THEIR TREATMENT IN AERATION TANKS.

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VODGEO

On the basis of examinations carried out at the Institute VODGEO waste waters from oil-refining plants after being treated in aeration tanks were found still toxic. To prevent their detrimental effect on acquatic life they must be diluted I6-60 times.

Up to now it was not possible to answer what determines this toxicity and what kind of substances present in waste water is toxic.

We should note that oil-containing waste waters composition is changeable and depends on the degree of treatment, that is why for determination of organic substances in biochemically treated oil-containing waste water four methods of concentrating were used with the simultaneous division of organic substances mixture into several groups depending on chemical composition of separate components: I) extraction by diethyl ether, 2) adsorbtion on activated carbon with desorption by various solvents, 3) distillation from alkaline medium with the application of freezing for neutral compounds concentrating, 4) distillation from acid medium with the application of the same freezing process for neutral compounds.

In all cases this division is based upon specific affinity of the mixture components towards solvents and on their various acidic and basic properties.

It had been stated before, that evolution of organic substances from biochemically treated oil-containing waste water by direct extraction method with diethyl ether and sorption on activated carbon leads for several reasons to the considerable loss of some part of volatile organic compounds. Besides, at direct extraction method too low degree of organic compounds removal from waste waters is obtained owing to the fact that many of these compounds have low distribution factor in the water - diethyl ether system.

Schemes developed by the authors were used in the investigations carried out for separating and concentrating of organic substances from waste water and for their division into groups.

According to these schemes waste water to be analysed is suggested to be subjected to thrice-repeated concentrating in order to raise extraction efficiency of organic substances from water by ether. Separation is commenced with the distillation of volatile bases and neutral compounds from alkaline or acid medium. Therevy all acids and phenols in the form of their salts remain concentrated in a small volume of the distillation residue. The distillation residue is being acidified and extracted repeatedly at water to ether ratio I:I. At such extracting practically all volatile acids are being evolved by ether. All oxy- and polyacids with the distribution factor =0.I polyalkohols, aminoacids, sulfoacids, sugars, urea remain in the water layer. Then separation of acids from phenols is being conducted, and after this in each group obtained further division on volatile and non-volatile substances is being carried on.

The group of organic bases is concentrated the same way. After acidification of the distillate in which volatile bases and neutral compounds are present, the latter are distilled and salts of volatile bases being repeatedly extracted by ether after acidification remain in the distillation residue in a small amount. And finally the group of neutral compounds is subjected to concentrating by freezing with their subsequent extraction with diethyl ether.

At a slow freezing losses of neutral compounds with ice were determined to make up no more than I0%. At a rapid freezing, when the solution is placed directly into the freezing chamber of the refrigerator, losses make up 40-50%.

The group of hydrophilic compounds (oxy- and polyacids, polyalkohols, sulfoacids, aminoacids, sugars, urea etc.) practically not extracted by ether (Their distribution factor = 0.I) is extracted at first together with the mineral salts and then after being evaporated dry is treated by dewatered ethanol for separation from mineral substances. This group of compounds may be subjected to further analysis for division into acids, bases and neutral compounds with the help of cephadexes and ion-exchange celluloses.

As a result of such treatment organic compounds from oil-containing waste waters treated are divided into four large groups: neutral, acidic, basic and hydrophilic compounds. These groups are divided in their turn into separate subgroups: volatile phenols, non-volatile phenols, volatile acids, non-volatile acids, including naphthenic acids, volatile organic bases, non-volatile organic bases, volatile and non-volatile neutral compounds. Quantitative characteristics of each separate group of compounds evolved are represented in Table I. Oil-containing waste water of an oil-refining plant was examined after being biochemically treated. The result of the analysis is given in Summary Table 2.

Analysis of the organic part of oil-containing waste water was not limited by determination of weight of separated groups of organic compounds: investigations

Table I Organic compounds in oil-containing waste water after biochemical treatment.

Separated groups of compounds			fluctuation of component during observation period mg/l (1971, 1972, 1973)
Neutral compounds	aldehydes and ketones		1.8–2.0
	oily substances		0.8–3.5
	quinones		0.3–1.1
	other neutral compounds		6.0–95
	The sume of neutral compounds		10–100
Acidic compounds	Strong organic acids	44–67	
	including: volatile		14–35
	non-volatile		20–53
	napthenic		2–4
	other non-volatile acids		16–51
	Very weak organic acids	6–8	
	phenols		0.1–3
	other very weak organic acids		5–8
	sum total of all acids		50–75
Basic compounds	Basic compounds in the form of hydrochloric salts		7–55
	Compounds soluble in water and not-extracted by ether (aminoacids, oxyacids, sulfoacids, polyalkohols, urea, sugars etc)		90–102
	Sum total of all organic compounds		150–330

Table 2 Summarized data of oil-containing waste waters chemical composition.

Ingredients defined	Waste water after sand filtration		Waste water after biochemical treatment
Colour	dirty-grey		light-yellow
Odour	oily		light oily
pH	6.9–7.3		7.2–7.6
COD mg 0/l	270–1050		80–120
BOD, mg 0_2/l	26–58		1.6–3.5
oil substances, filtrated, mg/l	–		0.7–3.5
oil substances, non-filtered, mg/l	18–64		1.5–5.0
Naphthenic acids, mg/l	8–20		2.0–4.7
Other non-volatile acids, mg/l	54–140		15–50
Volatile organic acids, mg/l	30–70		3.0–35
Volatile phenols with vapour, mg/l	1–11		0.01–3.7
Quinones, mg/l	–		0.3–1.1
Surfactants, mg/l	8–13		2.4–6.5
Dry residue, mg/l	8000–10000		4900–6000
Tempered residue, mg/l	7400–9300		4200–4800
Chlorides (Cl^-), mg/l	4900–6100		2700–3450
Phosphates (PO_4^{3-}) mg/l	–		0.6–0.8
Sulfates (SO_4^{2-}), mg/l	–		43–75
Nitrogen, ammonia mg/l	8–29		0.4–1.1
Nitrogen, nitrate mg/l	0.2–1.3	single determinations	7.8–8.4
Nitrogen, nitrite mg/l	0–0.1		0.03–0.33
Calcium, mg/l	660		100–370
Magnesium, mg/l	100		40–65
Sodium, mg/l	340		200
Potassium, mg/l	70		50

Waste water before treatment in aeration tanks is diluted by sewage 1.5 - 1.8 times.

were continued within each group. Two very important groups of compounds were tested in detail, that is neutral and acidic compounds, as they contain substances causing water toxicity (quinones, naphthenic acids).

Group of Neutral Compounds

The group contains a great number of separate components, namely non-oxidated hydrocarbones, ethers and esters, aldehydes, ketones, alkohols, quinones, anhydrides, lactones, fatty and aromatic halogen-bearing compounds.

Three groups of neutral compounds were analysed, namely neutral compounds evolved from water by direct extraction with diethyl ether; by sorption on activated carbon and by distillation from acidic and alkaline media with the subsequent concentrating by freezing. The latter method of neutral compounds separation indicated the presence of more considerable amount of organic compounds in the group as compared to those evolved by two other methods. At evolution of neutral compounds by above mentioned methods their contents in water were 21.5, 41 and 100 mg/l respectively. It brings the evidence to the fact, that the used method of concentrating of organic compounds by freezing after removal of acidic and basic groups of organic compounds gives us the possibility to preserve fully the high-volatile part of organic compounds, that is neutral compounds.

Analysis with the help of IR-spectroscopy has shown that adsorption spectra of these three groups of neutral compounds separated from water by various means (by extraction, sorption and distillation) did not differ greatly from one another. The three spectra were characterized by the presence of a large area of carbonyl compounds in them. Spectrum region at 1680 - 1780 cm^{-1} testifies to the presence of aldehydes, ketones, esters and lactones.

Gas chromatographic analysis of the neutral group of compounds indicated the presence of 16 components in it. In the group of neutral compounds substances mentioned below were extracted and defined (see Table I):

- aldehydes and ketones; their content in different water samples varied from 1.8 to 2.0 mg/l;
- hydrocarbons concentration from 0.8 to 3.5 mg/l;
- quinones concentration from 0.3 to 1.1 mg/l;
- the content of other neutral compounds in treated water was 6 - 95 mg/l.

This group also contains alkohols, esters, lactones.

Summing up the results of investigations of the composition of the neutral group it should be noted that the above-mentioned data testify to the fact that intermediate products of petroleum hydrocarbons biochemical oxidation, that is oxygen-containing compounds, are very numerous and present in water in considerable quantities.

Special attention should be paid to the high content of high-toxic and relatively stable quinones in waste water.

Quinones appear as intermediate products of aromatic hydrocarbons biochemical oxidation (oil from oil-refining plants bears up to 20% of aromatic hydrocarbons).

Examination of the neutral group composition should be completed by characteristics of those 10-15% of hydrocarbons resistabt to oxidation and remained in waste water after biochemical oxidation.

Having used a new gas chromatographic method of hydrocarbons determination with their distribution according to boiling temperatures the authors managed to define which of hydrocarbons remained in waste water after biochemical treatment.

The results of investigations given in Fig.I and in Table 3 illustrate hydrocarbons distribution according to their temperatures of boiling and testify to the fact that hydrocarbons boiling at temperatures lower than 2[illegible] - 300°C are practically absent in biochemically treated waste water. These hydrocarbons usually have up to C_{14} - C_{17} carbon atoms in the molecule. They are mainly oxidized, partly blown off in the course of treatment. The content of hydrocarbons boiling at higher temperatures decreases considerably as well. They remain in quantity of about 15-20% of their initial content.

Two chromatograms are given in Figure I. The first one (A) is given for waste water after sand filtration, that is before biochemical treatment. The chromatograms clearly demonstrate that before treatment oil-containing waste waters are polluted by raw oil, what can be seen from a fractional composition and uniform distribution of normal hydrocarbons peaks with a small incertion of their isomers and aromatic hydrocarbons.

As a result of treatment (see chromatogram "B") all volatile and isomeric hydrocarbons were removed from waste water - benzine and kerosene fractions are practically absent in waste water.

Fig. 2 demonstrates more clearly which hydrocarbons remain in waste water after biochemical treatment. Remaining hydrocarbons with 25 carbon atoms in the molecule give the highest peaks.

Summing up featuring of the neutral group of compounds it should be mentioned once more that this group is one of the largest judging by a number of components constituting it. It consists of toxic compounds along with non-toxic ones (aldehydes, ketones, anhydrides, esters and lactones).

Group of Acidic Compounds.

The group is divided into two subgroups: strong organic acids (acids with less than 10 carbon atoms in the molecule) and weak organic acids with pK value > 10.

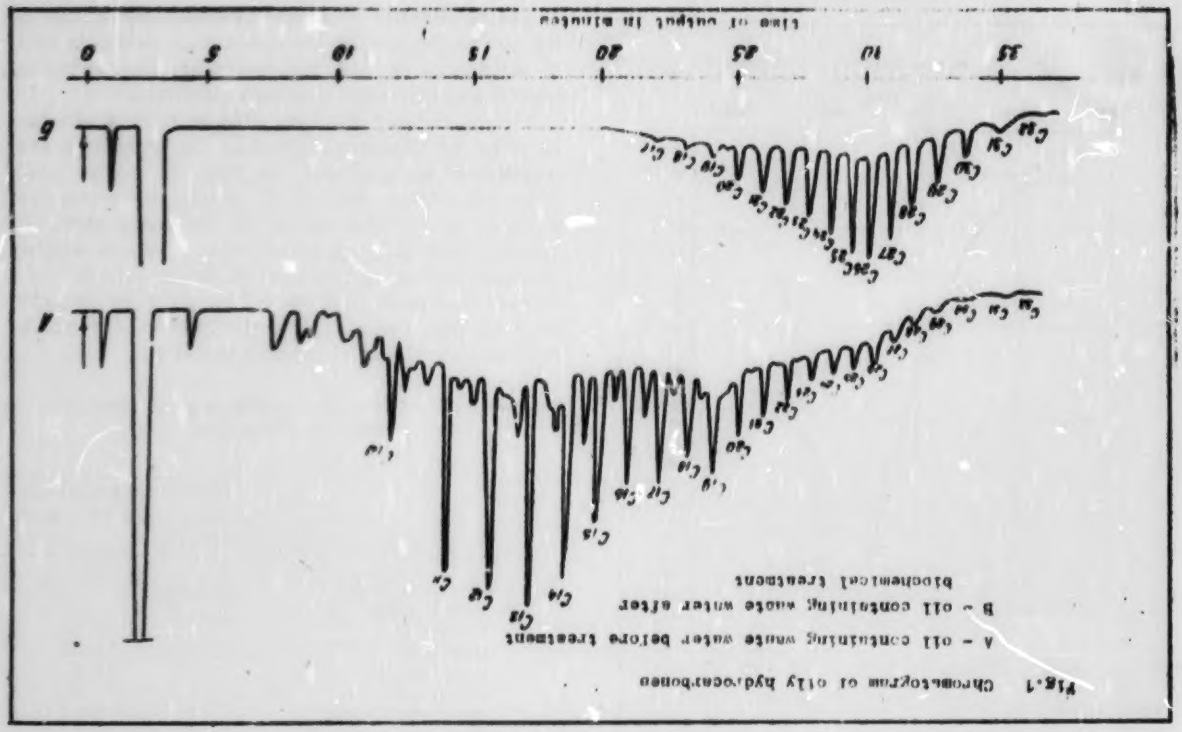

Fig.1 Chromatogram of oily hydrocarbons
A - oil containing waste water before treatment
B - oil containing waste water after biochemical treatment

Table 3. Distribution of hydrocarbons in oil-containing waste waters of an oil-refining plant according to boiling temperatures.

Number of fraction	Ranges of $T_{boil.}$ in °C	Waste water before treatment (after sand filteration)		Waste water after biochemical treatment	
		Hydrocarbons content		Hydrocarbons content	
		weight %	mg/l	Weight %	mg/l
1	100–130	1.5	0.57	–	–
2	130–160	3	1.14	–	–
3	160–190	4	1.53	–	–
4	190–220	13	4.95	–	–
5	220–250	13	4.95	5	0.18
6	250–280	19	7.24	5	0.18
7	280–310	13	4.95	10	0.35
8	310–340	11	4.20	10	0.35
9	340–370	11	4.20	18	0.63
10	370–400	6	2.29	22	0.76
11	400–430	2.5	0.97	11	0.39
12	430–460	1.5	0.57	9	0.32
13	460–490	1	0.38	5	0.17
14	490 and more	0.5	0.19	3	0.10
		100	38.2	100	3.5

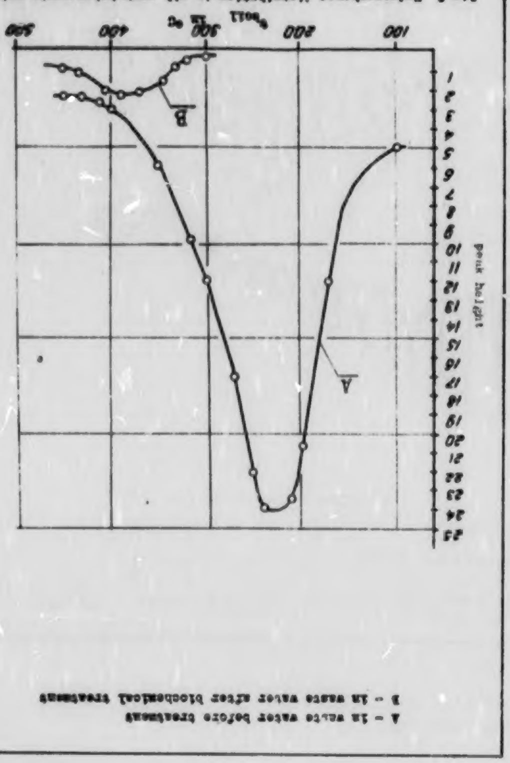

Fig.2 Hydrocarbones distribution in oil containing waste water according to boiling temperatures.

The group of acid compounds is the main one because biochemical processes proceed with the formation of acids. Various methods of analysis were used for its examination.

As a result of the examination carries out the total content of all acids, and non-volatile acids and volatile acids contents defined separately, the total content of innnocuous non-volatile acids and the content of some other acids were found.

Besides, the content of naphthenic acids and other highmolecular petroleum acids were determined. Summary data for organic acids content in waste waters are given in Table 4.

Formic, acetic, propyonic and butyric acids were found in all samples of oil-containing waste waters treated in aeration tanks in the course of low-molecular monocarboxylic acids determinations by a gas chromatigraphic method. Valeric and caproic acids were found only in one of the water samples. The fact that the content of acetic acid exceeds that of other acids and reaches 30-50% of all low-molecular monocarboxylic acids has appeared general for all water samples. These data are in agreement with the information on the role acetate plays in the metabolism of acquatic organisms.

Special attention was paid to the non-volatile acids as the contain both quite innocuous acids usually present in water sources, and high-molecular acids including naphthenic acids responsible for water toxicity.

Having analysed the data given in Table 4 one can come to the following conclusion: the group of acidic compounds has appeared, as expected, to be quite numerous (up to 30% of all organic compounds are included in it) and diverse by its composition. It contains acids differing in structure, molecular weight, chemical and physical properties. Strong organic acids content in it varies from 44 to 74 mg/1. From 20 to 50 mg/1 of this content fall to the share of non-volatile acids and only 2-4 mg/1 to naphthenic acids.

Table 4. Organic acids in oil-containing waste water after biochemical treatment.

	Fluctuations during observation period 1971, 1972, 1973 mg/1	
I. Strong organic acids	44 – 74	
a) Volatile acids	14 – 35	
formic acid		3 – 8
acetic acid		8 – 15
propionic acid		3 – 5
butyric acid		4 – 7
Other volatile acids calculating on valeric acid		–
b) Non-volatile acids	20 – 53	
naphthenic acids		2 – 4
lactic acid		1 – 4
amber acid		
fumaric acid		
glutaric acid		1 – 3
adipinic acid		
pyruvic acid		
oxalic acid		
malonic acid		1 – 4
and other not identified		
malic acid		
and other acids not identified		0.3–5
Other high-molecular acids		11–35
II. Very weak organic acids	6 – 8	
a) phenols (volatile with vapour)		0.–3
b) other very weak organic acids (phenols with the place substituted in p-position, estersof phenolic acids		5 – 6
Sum total of all organic acids		50 – 82

Summing up the results of analysis of organic compounds in biochemically treated oil-containing waste waters it should be mentioned once more that the composition of such waters is very changeable and depends on the degree of organic compounds biochemical oxidation.

The data obtained on waste waters being examined testify to the fact that ether-extracted compounds to which special attention had been attracted before, represent only a minute part of organic substances, in order of 35 mg/l or 10-15% of the total quantity of organic substances.

Conclusions

1. Analyses of chemical composition of oil-containing waste waters carried out in accordance with the new schemes for organic substances removal from waste waters permit to preserve all volatile compounds, while the methods considered before, such as direct extraction by diethyl ether and sorption on activated carbon led for different reasons to the loss of volatile substances.

2. It is shown that biochemically treated waste water contains substantial quantity of various oxygen-containing organic compounds besides hydrocarbons remained. Volatile, non-volatile acids, including naphthenic ones and neutral compounds, such as hydrocarbons, quinones, alkohols, aldehydes, ketones, alkohols, and esters were extracted and determined quantitatively. The total content of such hydrophilic compounds as sugars, aminoacids, oxyacids, sulfoacids, polyalkohols etc. in water was found along with the total content of organic bases. IR-spectrum and chromatograms indicated qualitatively several other substances as well.

3. It was reaffirmed that about 10-15% of initially present petroleum hydrocarbons remain in waste waters treated in aeration tanks. Gas chromatographic analysis has indicated that they belong to the compounds containing more than 14 carbon atoms in the molecule which is indicative of the absence of hydrocarbons of benzine and kerosene fractions in the waste water treated.

4. The investigations have shown that at biochemical treatment of oil-containing waste waters petroleum hydrocarbons undergo deep chemical changes. A considerable part of them in the form of intermediate products of different degree of oxidation remains in the waste water and causes high COD value of waste waters treated (in order of 100-150 mg 0/1) and their toxicity. It was found that the following compounds are responsible for toxicity of biochemically treated oil-containing waste water:

- quinones containing in waste water at concentration up to 1 mg/l, which 10 times exceeds maximum permissible concentrations,
- neutral compounds at concentration of 25 mg/l and more that also exceeds their non-toxic level. Toxicity of this group is caused apparently, to a considerable extent, by the presence of quinones in it,
- minerals salts (water salinity ≥ 5 g/l),
- phenols, reduced to quinones as a result of biochemical oxidation.
- As the toxicity of ciochemically treated waste water decreases and even fully disappears with the time passes, detention of treated waste waters in ponds before being discharged is considered to be advisible.

COMPARISON OF ALTERNATIVE STRATEGIES FOR COKE PLANT WASTEWATER DISPOSAL

by ROBERT W. DUNLAP Professor of Engineering and
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Trends in Coke Making

Fifty years ago, the production of coke from by-product ovens first surpassed the production from beehive ovens. For many of these same years, the by-product process was praised for two significant advances over beehive coking; first, the fact that by-product processing introduced significant chemical recovery into coke making and second, that by-product processing significantly reduced air pollution problems associated with coking. The last 20-25 years, however, have brought a changed perspective. While oven-coke production has remained stable at 54-64 million metric tons per year over the last quarter century, chemical recovery has grown increasingly less advantageous. In 1950, twenty-two percent of product values from the coke plant were associated with the value of coal chemicals[1]. By 1973, coal chemicals represented only twelve percent of total product value. At the same time these changes were taking place, increasing attention has been focused on the other principal difference between by-product and beehive coking, namely the introduction of significant water pollution problems which are a direct consequence of the gas processing.

Effluent Guidelines

Coke plant effluent limitations have been imposed by the Environmental Protection Agency[2]. It is recognized that coke plant wastewaters are typically as saline as sea water and contain a broad range of organics. Limitations are set for oil and grease, suspended solids, pH and sulfides, but the principal attention for the guidelines are for the control of ammonia, cyanide and phenolics. By 1977, the guidelines call for more than 90 percent reduction of these pollutants from the levels in typical untreated process waters. Further control by 1983 is expected to reduce discharges of the three by more than 99 percent (Table A).

TABLE A
Effluent Limitations for Selected
Coke Plant Pollutants (as kilograms)
per million kilograms of coke)

Pollutant	Typical Raw Wastewaters	BPCTCA (1977)	BATEA (1983)
Ammonia	914	91.2	4.2
Cyanide	120	21.9	0.1
Phenol	262	1.5	0.2
Average Percent Removal	0.0%	91.2%	99.7%

The intent of this study is to address the coke plant wastewater problem by examining a number of topics. What are the specific sources of the wastewaters? Can they be reduced in quantity through process changes? How do process objectives and environmental demands like control of air pollution influence waste characteristics? How can we evaluate the environmental impacts to air, water, and land which result from process effluents or are associated with the energy demands of process control?

Coke Plant Wastewater Sources

By-product coke plants vary widely in size, extent and type of by-product recovery, and wastewater practices. Wastewaters in coking originate from three principal sources: coal moisture, water of decomposition, and process waters added during gas treatment and by-product recovery. The process waters are the largest fraction of the total wastewaters and typically account for 60 to 85 percent of the total flow, which may range from 500 to 1700 liters per metric ton depending on the level of process water recycle. Typical gas processing and recovery steps are shown in Figure A, which indicates the six categories of wastes normally identified; (1) tar still wastewater, (2) excess or waste ammonia liquor (WAL) from the primary cooler, (3) ammonia absorber and crystallizer blowdown, (4) final cooler wastewater blowdown, (5) light oil (Benzol) plant wastewater, (6) gas desulfurizer and cyanide stripper wastewater. Table B indicates the level of wastewater flow and mass emissions of cyanide, ammonia, and phenol for each of the wastewater streams. Loose or tight recycle is a measure of the flow reduction achieved through recycle and process modification in the final cooler and the benzol plant. Mass emissions are essentially the same for both configurations with the exception of some loss of pollutants assumed for tight recycle due to by-product contamination, volatilization to the atmosphere in open cooling towers, and development of corrosion products in the coke oven gas distribution system.

The environmental impact of these wastewater streams can be summed up by considering the overall mass balance of emissions to the air, water, and the land. The coke plant necessarily consists of coke ovens, the quench towers for the incandescent coke, the by-product plant, and an associated wastewater plant to treat the wastes to meet the guidelines. Figure B shows the principal plant input, coal, and the main outputs of

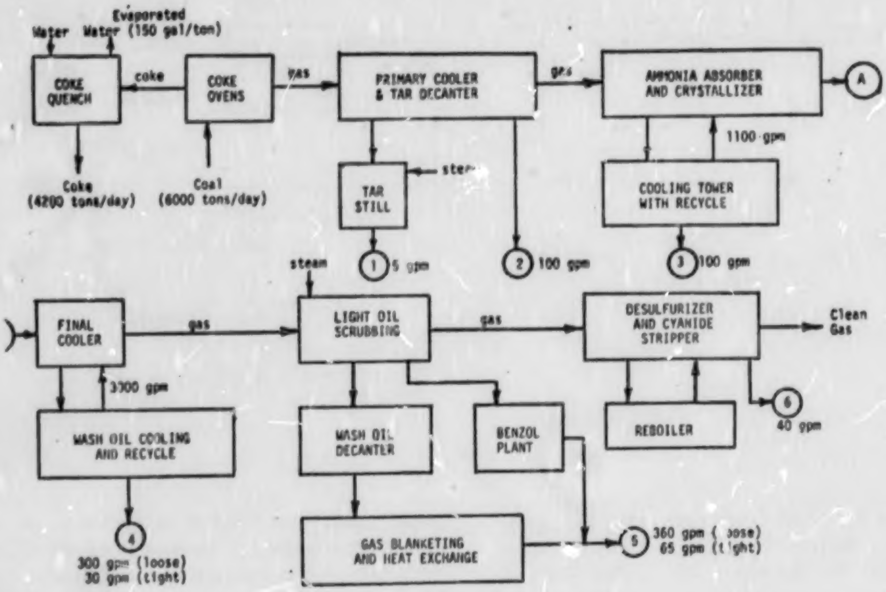

Water
Evaporated Water (150 gal/ton)
COKE QUENCH
coke
COKE OVENS
gas
PRIMARY COOLER & TAR DECANTER
gas
AMMONIA ABSORBER AND CRYSTALLIZER
A
1100 gpm
Coke (4200 tons/day)
Coal (6000 tons/day)
TAR STILL
steam
COOLING TOWER WITH RECYCLE
1 5 gpm
2 100 gpm
3 100 gpm
steam
FINAL COOLER
gas
LIGHT OIL SCRUBBING
gas
DESULFURIZER AND CYANIDE STRIPPER
Clean Gas
3300 gpm
WASH OIL COOLING AND RECYCLE
WASH OIL DECANTER
BENZOL PLANT
REBOILER
6 40 gpm
4 300 gpm (loose) 30 gpm (tight)
GAS BLANKETING AND HEAT EXCHANGE
5 360 gpm (loose) 65 gpm (tight)

Figure A. Schematic of Coke Plant Wastes.

Table B. Characteristics of Coke Plant Wastewater Streams
Basis: 5443 kkg/day coal charged at 10% moisture
with 70% coke yield, equivalent to
3810 kkg/day coke product.

				Mass Flow	
Flow tiwh Loose Recycle	Flow (gpm)	(lpm)	Cyanide (kg/day)	Ammonia (kg/day)	Phenol (kg/day)
1. Tar Still	5	20	2	136	132
2. WAL	100	380	33	3270	794
3. NH_3 Crystallizer	100	380	8	6	2
4. Final Cooler	300	1140	164	65	63
5. Benzol	360	1360	4	6	10
6. Desulfurizer	40	150	246	0	0
Total	905	3430	457	3483	1001

				Mass Flow	
Flow with Tight Recycle	Flow (gpm)	(lpm)	Cyanide (kg/day)	Ammonia (kg/day)	Phenol (kg/day)
1. Tar Still	5	20	2	136	132
2. WAL	100	380	33	3270	794
3. NG_3Crystallizer	100	380	8	6	2
4. Final Cooler	30	110	82	33	40
5. Benzol	65	250	2	2	3
6. Desulfurizer	40	1150	246	0	0
Total	340	1290	373	3447	971

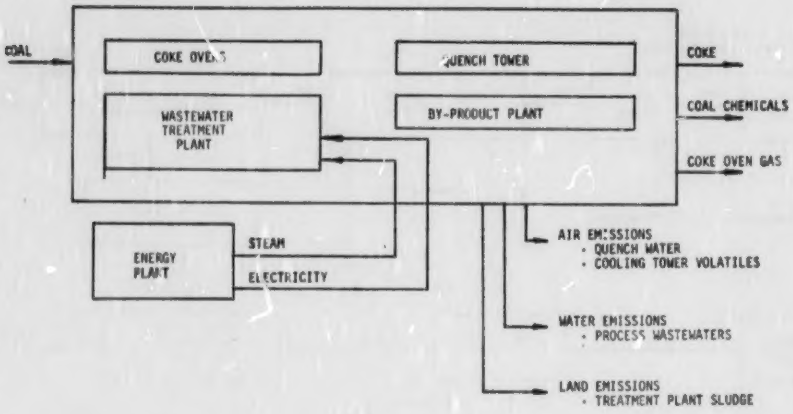


FIGURE B

coke, coal chemicals, and coke oven gas. The mass balance must also include air emissions from the open cooling tower and the quench tower in the form of volatiles and particulate matter. Water emissions may be adequately represented by ammonia, cyanide, and phenol. To control the wastewater effluents to the degree required by current regulations, a new element must be added–energy in the form of steam and electricity is needed to operate the treatment systems.

Energy for Wastewater Control–Alternate Strategies

The energy system is examined more closely in Figure C. It consists of a power plant, assumed to be a coal-fired boiler, to raise steam and to generate electricity for the wastewater treatment plant. The power plant also produces environmental emissions even though the plant is configured to meet applicable air and water regulations. Particulate matter, sulfur dioxide, nitrogen oxides, and waste heat are emitted to the air. Waste heat goes to the water, while land emissions are ash and SO_2 scrubber sludge from the power plant, as well as demineralization or softening sludge from the boiler water treatment plant. An interesting problem now arises. It appears that as one problem is solved–the wastewater effluent problem from the coke plant–another emission problem is created, namely the disposal of effluents produced from generation of the required steam and electricity. Furthermore, it seems obvious that more and more energy will be required as the level of wastewater treatment becomes more stringent. To decrease the effluents from the coke plant, one must the boiler plant. Several questions are posed. Are we working at cross purposes? What is the net environmental impact? How do we obtain an optimum level of wastewater treatment which achieves the maximum environmental improvement, considering all effects? To answer these questions it is necessary to perform a careful environmental assessment of the coking operation, including an examination of alternate strategies for handling the wastewaters. Table C lists eight alternate strategies (Cases 0 through 7) for controlling wastewater discharges. Each strategy involves one of three levels of wastewater treatment (Raw wastewater, Level I, Level II), one of two levels of recycle (Loose, Tight), and one of two quenching practices (Clean, Wastewater).

Flow processes for the wastewater treatment strategies are shown in Figures D & E for a hypothetical coke plant configured for this study. The wastewater flows are generated from recovery operations found in many steel plants. With a daily coal charge of 6000 tons (5443 kkg) and a daily furnace coke production of 4200 tons (3810 kkg), such a plant would be among the largest 25 plants in the country. Level I treatment is wholly a physical-chemical system employing a method of cyanide stripping based on existing technology developed by Bethlehem Steel Corporation[3], ammonia removal using a conventional still, and phenol extraction based on existing technology developed by Jones and Laughlin Steel Corporation[4]. Level II is a higher level of treatment, combining physical-chemical operations with biological waste treatment. The biological plant is similar to an existing facility at Bethlehem Steel and is designed to reduce the carbonaceous oxygen demand, with performance primarily set for phenolics reduction. These treatment systems do not precisely correspond to treatment levels designed to meet current EPA BPCTCA or BATEA limits. However, Level I meets BPCTCA guidelines for cyanide and ammonia; Level II meets all BPCTCA guidelines and the BATEA guideline for phenol.

The eight different control strategies each result in pollutant emissions to the air, water, and land. Air emissions originate from the coke quench tower, from

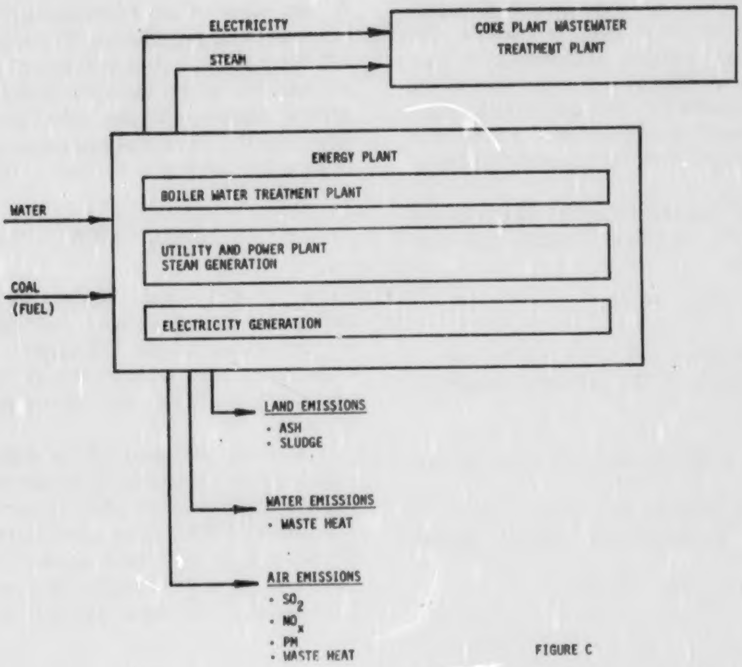

ELECTRICITY
STEAM
COKE PLANT WASTEWATER TREATMENT PLANT
ENERGY PLANT
BOILER WATER TREATMENT PLANT
UTILITY AND POWER PLANT STEAM GENERATION
ELECTRICITY GENERATION
WATER
COAL (FUEL)
LAND EMISSIONS
• ASH
• SLUDGE
WATER EMISSIONS
• WASTE HEAT
AIR EMISSIONS
• SO_2
• NO_x
• PM
• WASTE HEAT

FIGURE C

Table C. Coke Plant Wastewater Control Strategies

Case	Treatment	Level of Recycle		Type Quency	
		Loose	Tight	Clean	Wastewater
0	Raw Wastewater	X		X	
1	Raw Wastewater	X			X
2	Raw Wastewater		X	X	
3	Raw Wastewater		X		X
4	Level I		X	X	
5	Level I		X		X
6	Level II		X	X	
7	Level II		X		X

the open cooling towers, and from the power plant supplying electricity and/or steam to the treatment process units. Water emissions arise from coke plant wastewaters, from blast furnace wastewaters which account for pollutants transferred by wastewater quenching, and from power plant waste heat discharges. Land emissions originate at the power plant, the quench tower, the boiler water treatment plant, the coke plant ammonia still, and the coke plant biological treatment plant.

The foundation of the analysis is the construction of an inventory of all principal pollutants emitted to air, water, and land for each of the selected control strategies. Figure F shows the daily emissions for a selected list of pollutants from each of the active operations for each control strategy. Measures were generated for eight pollutants emitted to the air, six pollutants to the water, and five pollutants to the land. By itself, this accounting of the residuals shows the relative complexity of the problem. It remains for the community and the regulatory agency to develop an aggregate summation of these different residuals in order to select an overall best strategy for the environment as a whole.

Cross-Media Analysis

Comparing the complete inventory of emissions with the original wastewater loads (Figure F, Case 0) shows that the reduction of emissions of ammonia, cyanide, and phenol to the water involves the generation and discharge of many other pollutants and treatment residuals to the air and land. A comparison of the relative environmental impact of the different strategies demands the ability to compare trade-off effects, i.e., the effect on the environment of reducing mass emissions of pollutants to the water while increasing mass discharges of other pollutants to the air and land. Reiquam, Dee, and Choi at the Battelle Memorial Institute under a contract sponsored by the Council on Environmental Quality and the EPA developed a technique for this purpose, termed Cross-Meida Analysis[5]. This analysis starts with a mass emission inventory. A hierarchical arrangement of weights is developed consisting of two levels, media weights and pollutant weights.

The first level of weights for air, water, and land may be regional or applicable to the country as a whole. The second level of pollutant weights establishes a mechanism for allocating relative fractions of each of the media weight totals to each pollutant. Choices between alternate strategies are based on the relative values of a numerical index calculated from the Cross-Media Analysis.

The environmental degradation index (EDI) is the arithmetic sum of the weighted damages for each pollutant in each media,

$$EDI = \Sigma_p d_{p,s} W_p M_p$$

where p is the pollutant index and

$d_{p,s}$ is the damage function for a selected strategy, s, with

$(0 < d_{p,s} < 1)$.

M_p is a modifier function which accounts for the dispersal and

persistence of the pollutant $(0.1 < M_p X\, 0.8)$.

W_p is the weight assigned to the pollutant, p, relative to the

other pollutants $(\Sigma_p W_p = 1000)$

A large value of the EDI means a large expectation of environmental degradation. Of course, the nature of the weighting scheme does not permit one to interpret the number absolutely. However, it is useful for comparing various control strategies. The algebraic difference between $(EDI)_0$ for a base case strategy and the $(EDI)_s$ for some other strategy is defined as the strategy effectiveness index $(SEI)_s$:

$$(SEI)_s = (EDI)_0 - (EDI)_s$$

Values of SEI which are positive are interpreted as having a net improvement over the base case, while negative values of the SEI imply a net environmental degradation. This value of the SEI is the final basis of comparing, ranking, and choosing between control strategies.

This study used two sets of pollutant weights. One was based on choices made by steel industry experts at Battelle Institute (BMI) while the second was selected by the authors (CMU) from a consideration of several sets of national air and water quality criteria[6,7] Table D compares the relative weights. Both sets of choices assign approximately the same emphasis to each media, with

Figure D. Flow Diagram for Treatment Level I for Wastes from Tight Recycle

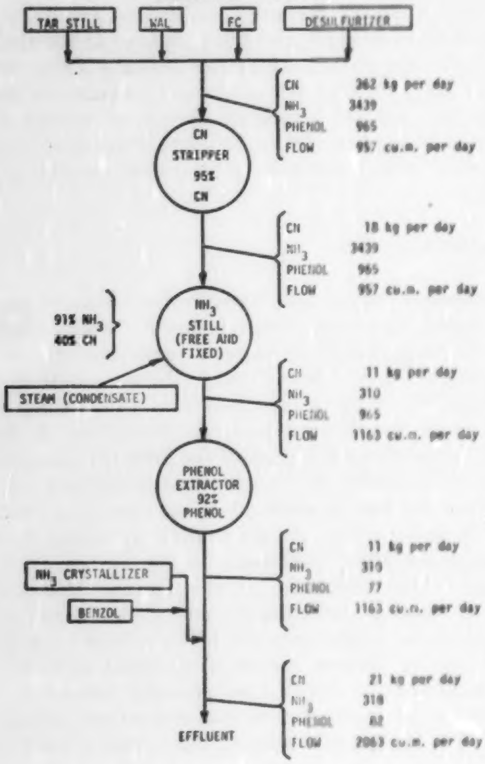
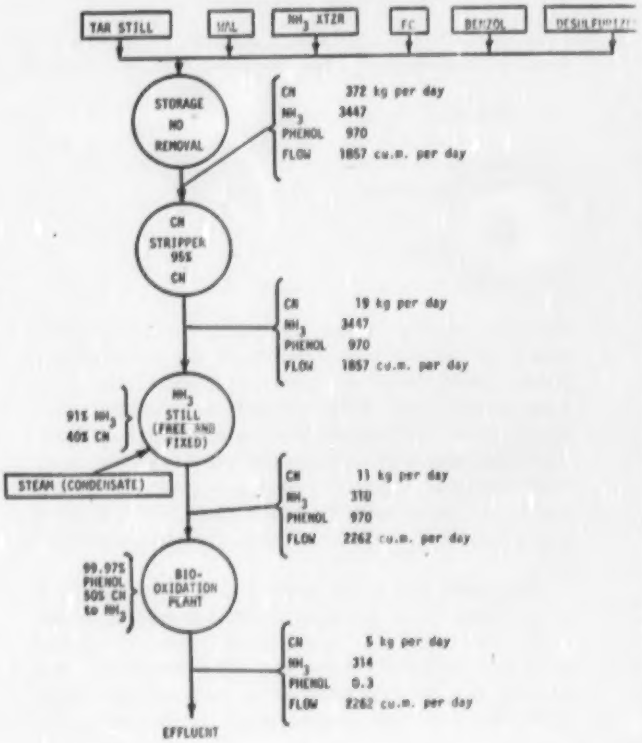

TAR STILL
WAL
FC
DESULFURIZER
CN 362 kg per day
NH3 3439
PHENOL 965
FLOW 957 cu.m. per day
CN STRIPPER 95% CN
CN 18 kg per day
NH3 3439
PHENOL 965
FLOW 957 cu.m. per day
91% NH3
40% CN
NH3 STILL (FREE AND FIXED)
STEAM (CONDENSATE)
CN 11 kg per day
NH3 310
PHENOL 965
FLOW 1163 cu.m. per day
PHENOL EXTRACTOR 92% PHENOL
CN 11 kg per day
NH3 310
PHENOL 77
FLOW 1163 cu.m. per day
NH3 CRYSTALLIZER
BENZOL
CN 21 kg per day
NH3 318
PHENOL 82
FLOW 2063 cu.m. per day
EFFLUENT

Figure E. Flow Diagram for Treatment Level II for Wastes from Tight Recycle


TAR STILL
WAL
NH3 XTZR
FC
BENZOL
DESULFURIZ
STORAGE NO REMOVAL
CN 372 kg per day
NH3 3447
PHENOL 970
FLOW 1857 cu.m. per day
CN STRIPPER 95% CN
CN 19 kg per day
NH3 3447
PHENOL 970
FLOW 1857 cu.m. per day
91% NH3
40% CN
NH3 STILL (FREE AND FIXED)
STEAM (CONDENSATE)
CN 11 kg per day
NH3 310
PHENOL 970
FLOW 2262 cu.m. per day
99.97% PHENOL 50% CN to NH3
BIO-OXIDATION PLANT
CN 5 kg per day
NH3 314
PHENOL 0.3
FLOW 2262 cu.m. per day
EFFLUENT

air and water both ranked above the land. The CMU system distributes the pollutant weights less evenly than BMI and focuses on phenol in water as being the most critical pollutant to control.

The mass emission inventory shown graphically in Figure F must be converted to a set of numbers between 0 and 1, to be expressed as the damage function, d_n, for the cross-meida analysis. This study examined the sensitivity of the environmental degradation index to the procedure used for calculating damage. The simplest damage function imaginable scale damage as a linear function of the mass of pollutant discharged. One may choose damage functions to scale relative emissions non-linearly, so as to place heavy damage on any small emission or to delay assignment of damage until a large fraction of the largest possible emission is reached (Figure G). The results of the sensitivity of the relative rank of the coke plant strategies for nine damage functions are shown in Table E. Using either the CMU or the BMI weighting functions and the various damage functions, the relative ranks of the coke plant wastewater strategies are nearly the same. By comparing absolute values of the SEI calculations as well as the sensitivity of the ranks for each strategy, it is possible to assemble a qualitative grouping of the coke plant strategies shown in Table F.

Comparison of Wastewater Control Strategies

Table G shows that control of coke plant wastewaters does result in environmental improvement for the watercourse to which the plant discharges its wastes. Control strategy Case O (loose recycle, no wastewater treatment, discharge to the river) is chosen as the base case against which all other strategies are compared. The least desirable control strategies have negative SEI values, indicating a net environmental damage compared to the base case. In contrast, a large positive total SEI value for a control strategy indicates net environmental improvement compared to the base case. For all control strategies, and either weighting method, positive SEI values occur for the water media, indicating environmental improvement over the base case.

Note, however, that environmental improvement for the watercourse is coupled in every situation with degradation of the air and land media. Values of zero for the SEI mean that these cases are identical to the base case. Furthermore, in some cases the net environmental degradation of the air and land media are large enough to negate the improvement which has taken place in the watercourse. Environmental improvement in one media - here, water - is inextricably associated with deleterious

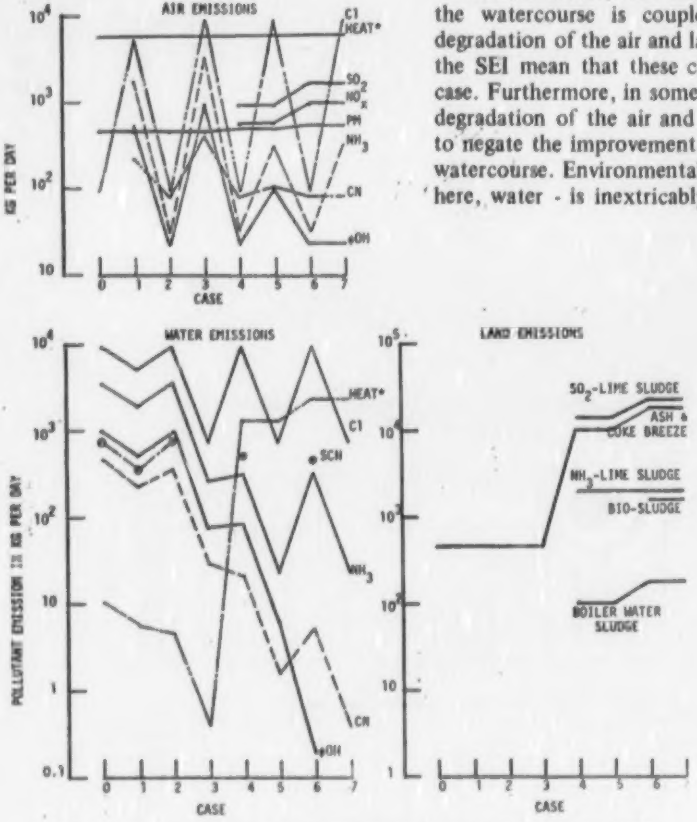


FIGURE F. EMISSIONS INVENTORY FOR 3810 KKG/DAY (4200 TON/DAY) COKE PLANT FOR EIGHT SELECTED STRATEGIES.

*HEAT IN 10^6 BTU PER DAY

Table D. Pollutant Weights (W_p) and Modifier Function (M_p) for Coke Plant Wastewater Study

	CMU Weights			BMI Weights		
Pollutant	W_p	M_p	W_pM_p	W_p	M_p	W_pM_p
To Water:						
NH_3	5	0.6	3	52	0.6	31
φOH	321	0.5	160	84	0.5	42
CN	22	0.5	11	74	0.5	37
SCN	3	0.5	2	56	0.5	28
Cl	1	0.6	1	33	0.6	20
Heat	22	0.5	11	74	0.5	37
Sum	374			373		
To Land:						
Ash, Coke Breeze	41	0.5	20	42	0.5	21
SO_2-Lime Sludge	54	0.6	32	58	0.6	35
NH_3-Lime Sludge	54	0.6	32	58	0.6	35
Boiler Water Sludge	54	0.6	32	58	0.6	35
Biological Sludge	54	0.6	32	58	0.6	35
Sum	255			274		
To Air:						
NO_x	30	0.5	15	22	0.5	11
SO_2	70	0.7	49	43	0.7	30
PM	60	0.8	48	56	0.8	45
NH_3	26	0.5	13	47	0.5	24
φOH	48	0.4	19	56	0.4	22
CN	82	0.4	33	60	0.4	24
Cl	25	0.4	10	47	0.4	19
Heat	30	0.5	15	22	0.5	11
Sum	371			353		
Total	1000			1000		

Table E. Frequency Distribution of Alternative Strategies by Rank for Nine Damage Function Choices

Number of Times Case Ranked As Shown (CMU Weights)

Rank / Case	1	2	3	4	5	6	7	8	Average Rank
0	X	1	X	2	2	3	1	X	5.00
1	1	1	X	4	1	1	1	X	4.11
2	X	X	X	1	5	3	X	X	5.22
3	6	1	X	2	X	X	X	X	1.78
4	2	4	2	X	1	X	X	X	2.33
5	X	2	7	X	X	X	X	X	2.78
6	X	X	X	X	X	2	7	X	6.78
7	X	X	X	X	X	X	X	9	8.00

Number of Times Case Ranked As Shown (BMI Weights)

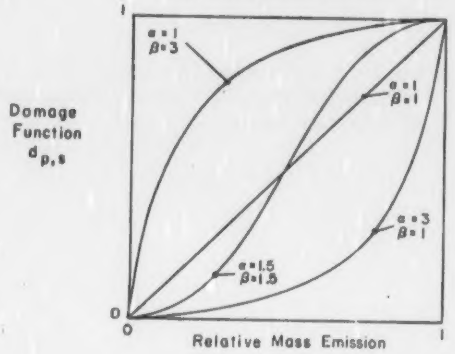
Rank / Case	1	2	3	4	5	6	7	8	Average Rank
0	X	2	1	X	1	5	X	X	4.67
1	3	2	1	X	3	X	X	X	2.78
2	X	X	2	2	5	X	X	X	4.33
3	6	2	X	1	X	X	X	X	1.56
4	X	X	1	4	X	4	X	X	4.78
5	X	3	4	2	X	X	X	X	2.89
6	X	X	X	X	X	X	X	9	8.00
7	X	X	X	X	X	X	9	X	7.00

TABLE F

Grouping of Wastewater Treatment Strategies

Case	Treatment	Qualitative Ranking
3	Raw wastewater effluent; tight recycle; wastewater quench	Preferred
5	Level I treatment; tight recycle; wastewater quench	Preferred
1	Raw wastewater effluent; loose recycle; wastewater quench	Better than Base Case
4	Level I treatment; tight recycle; wastewater discharge to watercourse	
2	Raw wastewater effluent; tight recycle; wastewater discharge to watercourse	Base Case
0	Raw wastewater effluent; loose recycle; wastewater discharge to watercourse	
6	Level II treatment; tight recycle; wastewater discharge to watercourse	Not Preferred
7	Level II treatment; tight recycle; wastewater quench	

Figure G. The Damage Function.



The damage function is assumed to be the cumulative Beta Function based on two parameters, α and β.

Mean of distribution is $[\alpha/(\alpha + \beta)]$ and the variance of the distribution is $[\alpha\beta/(\alpha + \beta)^2 (\alpha + \beta + 1)]$.

For all cases, the damage function is 1 when the relative emission is 1, that is the actual emission is maximum. When the actual emission is zero, the damage function is zero.

The following ranges of α and β were studied:

α \ β	1.0	2.0	3.0
1.0	X	X	X
2.0	X	X	X
3.0	X	X	X

TABLE G

Net Environmental Impact for Two Selected Sets of Pollutant Weights and a S–shaped Damage Function

(a = B = 1.5)

STRATEGY EFFECTIVENESS INDEX (CMU Weights)

Case	Air	Water	Land	Total	Rank
0	0	0	0	0	5
1	–39	85	0	46	4
2	– 5	3	0	– 2	6
3	–75	172	0	97	1
4	–16	162	– 70	76	2
5	–30	170	– 70	70	3
6	–28	164	–148	–12	7
7	–39	166	–148	–21	8

STRATEGY EFFECTIVENESS INDEX (BMI Weights)

Case	Air	Water	Land	Total	Rank
0	0	0	0	0	5
1	–47	77	0	30	2
2	– 3	5	0	2	6
3	–89	154	0	65	1
4	–12	92	– 76	4	4
5	–34	136	– 76	26	3
6	–20	82	–161	–99	8
7	–40	120	–161	–81	7

cross-media effects, which may be large enough themselves to provide no net environmental improvement for the control effort.

Conclusions

The prinicpal findings of this study apply to the coke plant problem in particular, but suggest there may be grave consequences whenever there is stringent effluent regulation for separate media. Wastewater treatment provides environmental improvement for one media, water, but will lead to the degradation of the other media, air and land. This is the phenomenon of cross-media impact; energy requirements for treatment processes create new pollutant residuals which are smeared across all media. For some wastewater treatment practices, the net environmental improvement due to the practice is negative, i.e., cross-media effects are so large as to negate the beneficial effects of improving the water media. The frequency for which net degradation of the environment is forecast from this analysis depends on input parameter values and assumptions; this frequency rises sharply with the stringency of wastewater treatment.

It is useful to characterize the coke plant problem in three ways - by type of quench water, by level of process water recycle, and by level of treatment selected for wastewaters. The cross-media analysis leads to the following observations:

- Quenching with coke plant effluents, regardless of their level of treatment, appears to be a preferred practice for the greatest net improvement of the environment. This practice is preferred over discharge of that effluent (at the same level of treatment) to watercourse.
- Tight recycle of cooling waters rather than loose recycle appears to be preferred for the greatest net environmental improvement.
- For the wastewater control case in which tight recycle of cooling waters is employed and the final effluent is used for wastewater quenching, no wastewater treatment is a preferred practice over either Level I or Level II treatment, if the greatest net environmental improvement is to achieved.
- For the wastewater control case in which tight recycle of cooling waters is employed and the final effluent is discharged to a watercourse, Level I is the preferred wastewater treatment, if the greatest net environmental improvement is to be realized. For this case, this treatment level is preferred over the alternatives of no treatment of Level II treatment.
- These results suggest that the current EPA effluent standards for by-product coke plants, particularly the BATEA (1983) limits, are too stringent to maximize the net environmental improvement which can result from the treatment and disposal of coke plant wastewaters.

The results of this study clearly support the contention that levels of environmental control must be considered very carefully if maximum improvement of the environment is to take place; stringent control of emissions is not necessary the best course of action. However, this analysis, like all analyses, is an approximation of reality, and not reality itself. In particular, the cross-media technique requires many assumptions which are open to question and interpretation. Nevertheless, the results of the study appear robust enough that strong conclusions can be stated regarding current by-product coke plant effluent limitations. This analysis is offered not to exacerbate the current controversy regarding treatment and disposal of coke plant wastewaters but to move the controversy toward more rational emphasis on net improvement of the environment, rather than emphasis on single media regulations and solutions.

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STUDIES ON OXIDATION PROCESSES OF CIANIDES AND PHENOLS IN WASTE AND NATURAL WATERS BY USING CHLORINE DIOXIDE.

by A.N. Belevtzev, Ju.L. Maximenko.

Hypochlorite, chlorine and chloride of lime are usually used as bactericidal and oxidizing agents in water and waste treatment processes. However their usage doesn't often produce significant effect.

Therefore the intensive searches of new oxidizing and bactericidal agents for water treatment are lately carrying out. At the institute VODGEO it was studied the possibility of chlorine dioxide utilization for above mentioned purposes in addition to testing for oxidation processes of various substances contained in natural and waste waters by using hypoclorites, ozone oxygen in the air and other oxidizing agents. This oxidazing agent was selected due to a number of its advantages over other oxidizing agents such as relative stability in water solutions, high oxidation potential.

In the performed tests the main attention was given to studyin the oxidation processes of simple and complex cyanides, rhodonides, sulfides and phenols because these compounds often occur in waste effluents of various industries and also in stream waters.

The considered compounds are strong toxic, posess offencive organoleptic properties and are converted to nontoxic ones during oxidation distruction.

The present paper deals with the results of investigations in the field of oxidation of cyanide and phenolic compounds.

Chemical effects of chlorine dioxide.

In the case chlorine dioxide interaction with reducers it gains 1 or 5 electrons and is reduced to chlorite or chloride ions that may be described by the following reactions (1 - 6):

$$ClO_2 + H^+ + e^- \rightleftarrows HClO_2 \qquad 1$$

$$ClO_2 + 4H^+ + 5e^- \rightleftarrows Cl^- + 2H_2O \qquad 2$$

$$ClO_2 + 2H_2O + 5e^- \rightleftarrows Cl^- + 4OH^- \qquad 3$$

$$HClO_2 + 3H^+ + 4e^- \rightleftarrows Cl^- + 2H_2O \qquad 4$$

$$ClO_2 + e^- \rightleftarrows ClO_2^- \qquad 5$$

$$ClO_2 + 2H_2O + 4e^- \rightleftarrows Cl^- + 4OH^- \qquad 6$$

On the basis of known normal redox potentials of the systems as 1 (E_0 = 1.27 v) and 2(E_0 = 1.5) and be using Luter's rule.

$$(m-p)\cdot E_{0\,m/p} = (m-n)\cdot E_{0\,m/n} + (n-p)\cdot E_{0\,n/p}$$

where m, n, p denote the degtee of valency and m > n > p

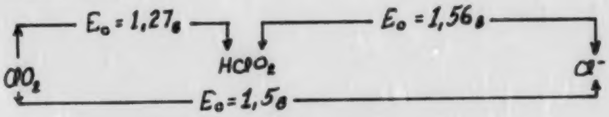
as well as by using Nernet's equation.

$$E_{\text{окисл/восст}} = E_{0\,\text{окисл/восст}} + \frac{0.059}{n} \lg \frac{(\text{окисл})(H^+)^m}{(\text{восст})}$$

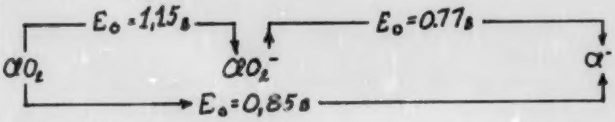
where n is the quantity of transfered electrons the normal redox potentials of systems as (3), (4), (5), (6) were estimated that proved to be equal respectively 0.84V; 1.56v ; 1.15v; 0.77v.

The conducted calculations allowed chlorine dioxide reduction to be presented in flow diagram in the following oxidation reactions as:

in acid media



in alkaline media



The schemes show that in acid media chlorine dioxide should be mainly reduced to chlorides as the redox potential of system CLO_2/CL = 1.5v more of that for systems $CLO_2/HCLO_2$ = 1.27v.

In alkaline media chlorine dioxide is reduced to chiorite ions at a faster rate as the normal redox potential of system CLO CLO_2 = 1.15v is more of that for system CLO_2/CL = 0.85v.

Insofar as the potential of redox reaction is a function of several other factors in the direction of reactions it may be deviations depending on particular conditions.

However the general regularity should be maintained. By using the normal redox potential we estimated the reaction potentials of chlorine dioxide interaction with oxidable substances under various conditions, thereby we selected the conditions of their carrying out, scheduled the proposed directions of reactions and their products.

Oxidation of cyanides

All the water soluble cyanides except for the complex cyanides of iron are very toxic compounds. As a rule cyanides affected by oxidizing agents are oxidized to cyanates as follows:

$$CN^- - 2\bar{e} + 2OH^- \longrightarrow CNO^- + 2H_2O \qquad 7$$

which are then hydrolyzed forming carbonate and ammonium ions that is described by the equation (8).

$$CNO^- + 2H_2O \longrightarrow CO_3^{2-} + NH_4^+ \qquad 8$$

The estimations based on determination of the reaction potential difference show that during the oxidation process of cyanides chlorine dioxide should be mainly reduced to chlorite ions as in alkaline media the potential difference of systems ClO_2/ClO_2^- and CNO^-/CN^- is more of that for systems ClO_2/Cl^- and CNO^-/CN^-.

The estimations were experimentally confirmed during cyanide oxidation of alkaline metals as well as cyanides bound to complexes with zinc and cadmium.

The results of researches showed that simple cyanides and cyanides bound to complexes with zinc and cadmium were oxidized to cyanates at the rate of chlorine dioxide described by the following equations as: (9), (10), (Fig. 1).

$$CN^- + 2ClO_2 + 2OH^- = CNO^- + 2ClO_2^- + H_2O \qquad 9$$

$$Me(CN)_4^{2-} + 8ClO_2 + 10\,OH^- = 4CNO^- + 8ClO_2^- + Me(OH)_2 + 4H_2O \qquad 10$$

where Me = Zn^{2+} or Cd^{2+} (5, 2 mg per 1 mg of cyanide ions).

In strong alkaline media (pH > 10) the reactions proceed at faster rate. Oxidation of cyanides bound to complexes with copper followed otherwise. In spite of the fact that copper-cyanide complexes are more stable versus ones contained zinc and cadmium they are oxidized more readily at chlorine dioxide rate decreased almost by five times.

The process is effected in two consecutive stages, at first cyanides are oxidized to cyanates while chlorine dioxide is reduced to chlorite ions that's given by equation (11).

$$Cu(CN)_3^{2-} + 7ClO_2 + 8OH^- = 3CNO^- + 7ClO_2^- + Cu(OH)_2 + 3H_2O \qquad 11$$

then the formed chlorite catalytically oxidizes the rest cyanides thereby being reduced to chloride ions, as follows:

$$4Cu(CN)_3^{2-} + 7ClO_2 + 4\,OH^- + 2H_2O = 12CNO^- + 7Cl^- + 4Cu(OH)_2 \qquad 12$$

In summation the process may be reproduced by the following equation:

$$5Cu(CN)_3^{2-} + 7ClO_2 + 12\,OH^- = 15\,CNO^- + 7Cl^- + 5Cu(OH)_2 + H_2O \qquad 13$$

So on the basis of conducted investigations we may state that cyanides bound to complexes with copper are catalitically oxidized, as a result chlorine dioxide gains five electrons and is reduced to chlorides.

The rate of process significantly depends on quantity of copper in the complex.

The catalysis was found to take place if ratio /Cu/:/CN-/ corresponded to complexes respectively $Cu(CN)_3^{2-}$ and $Cu(CN)_2^-$

The catalysis was not observed in the presence of the complex $Cu(CN)_4^{3-}$ and of free cyanide ions in solution (Fig. 2).

The estimations of constants concerning complex instability and the experimental data allow the assump-

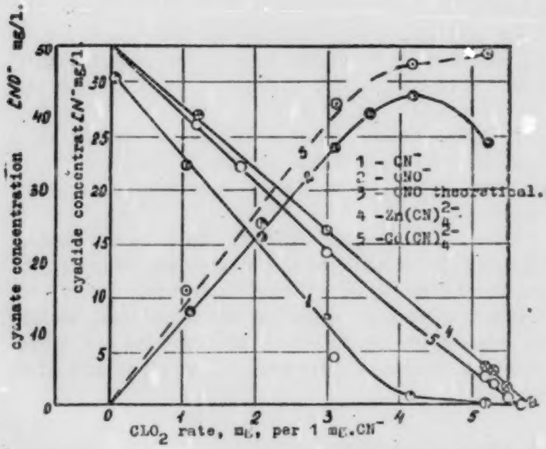


Fig.1. Effect of Chlorine Dioxide Rate on Oxidation Process of Cianides.

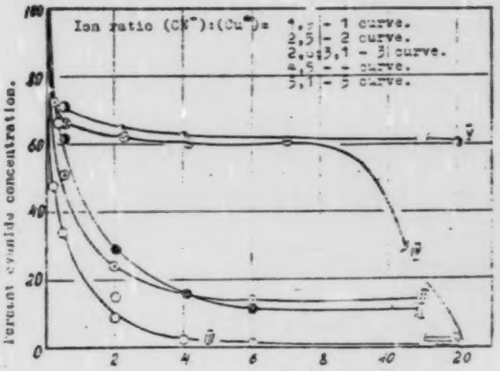


Fig.2. Effect ion ratio (CN⁻):(Cu⁺) on oxidation process of cyanides by chlorine dioxide.

tion to be made that the catalizators of process are itself copper-cyanide complexes $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$.

At introducing copper ions into solutions of complex cyanides of zince and cadmium the catalytic effect of copper-cyanide complexes on oxidation process was found out.

The oxidation process of cyanides bound to complexes with nickel and cobalt proceeds with great difficulties by the equation (14) and (15) when chloride dioxide rate is of much above the theoretical one (8-10 mg/mg)

$$Ni(CN)_4^{2-} + 8ClO_2 + 10OH^- = 4CNO^- + 8ClO_2^- + Ni(OH)_2 + 4H_2O \qquad 14$$

$$CO(CN)_6^{4-} + 12ClO_2 + 14OH^- = 6CNO^- + 12ClO_2^- + Co(OH)_2 + 6H_2O \qquad 15$$

It was due to large losses of CLO_2 as a result of its destruction caused by the low rate of oxidation process.

Chlorine dioxide cyanides bound to complexes with iron are not oxidized. Chlorine dioxide effect on ferrocyanides results in their oxidation only to ferrocyanides, i.e. oxidation of only metall in complex.

The formed cyanates produced from oxidation of cyanides are oxidized by chlorine dioxide with much more difficulty. The reaction occurs at marked rate only at pH < 6. The products of oxidation there to proved to be elementary nitrogen and bicarbonate ions.

So chlorine dioxide is reduced to chloride and chloride ions as:

$$10CNO^- + 6ClO_2 + 4H^+ = 10CO_2 + 5N_2 + 6Cl^- + 2H_2O \qquad 16$$

$$2CNO + 6ClO_2 + 2H_2O = 2CO_2 + N_2 + 6ClO_2^- + 4H^+ \qquad 17$$

At the same time hydrolysis of cyanates with subsequent formation of ammonium ions takes place at pH < 5. The rates of both processes are proportional at pH values in the range of 3.5 - 4.2.

Chlorine dioxide rate required for oxidation 1 mg of cyanate ion is a function of pH value. It is on average equal to 3.4 mg at pH values of 3.5-5.0, theoretical rate by the reactions (16) and (17) amounts respectively 0.96 mg/mg and 4.82 mg/mg.

Oxidation of phenolic compounds.

In complex problem of potable and waste water treatment the removing of phenols refers to category of technologic processes that require to be thoroughly investigated. Some of researches have studied phenol interaction with chlorine dioxide. However the obtained results are contradictory in many respects especially as concerns kinetics, mechanism and products of oxidation reactions.

The investigators of our country disclosed that in acid and neutral media phenol (carbolic acid) is readily oxidized by chlorine dioxide at the rate of 1.2 mg/mg (Figs. 3,4); the main products of oxidation is n6-benzoquinone.

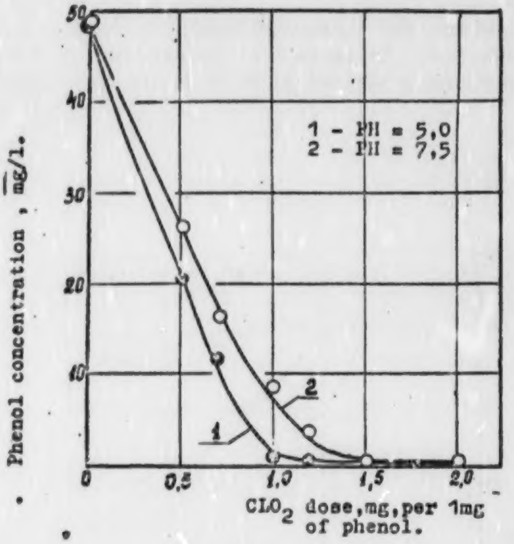


Fig.3. Phenol concentration variations vs.ClO$_2$ dose.

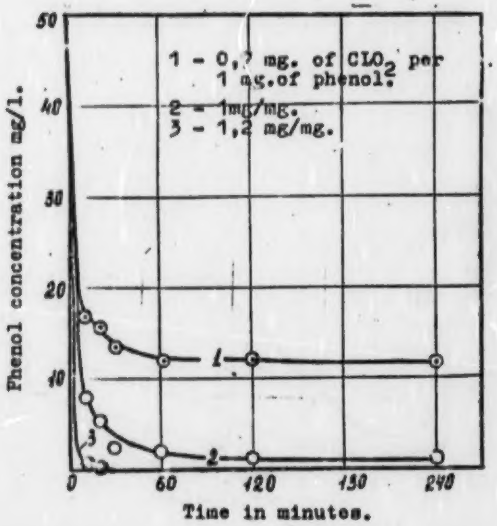


Fig.4. Kinetics of phenol oxidation by using various ClO$_2$ doses.

The oxidation rate and the required excess of chlorine dioxide are functions both of initial phenol concentration and of temperature.

Phenol concentrations vary from 50 to 0.02 mg/l while the rate of CLO_2 increases in the 1.2-2.7 mg/mg range.

Lowering the temperature results in decrease in reaction rate. An increase in reaction rate at low temperatures is achieved either by adding large quantities of CLO_2 (for complete oxidation of phenol at the temperature of 5°C the oxidizing agent is required to be 2-2.5 times of that at the temperature of 20°C) or by increase in time constant up to 4-6 hours (Figs. 5-6).

Mechanism of one especially depend on pH value and if in acid and neutral media the oxidation process occurs only to benzoquinone whereas in alkaline solution the reaction proceeds more deeply. Quinone formed at the first stage is then oxidized to carbonic acid (Figs. 7, 8).

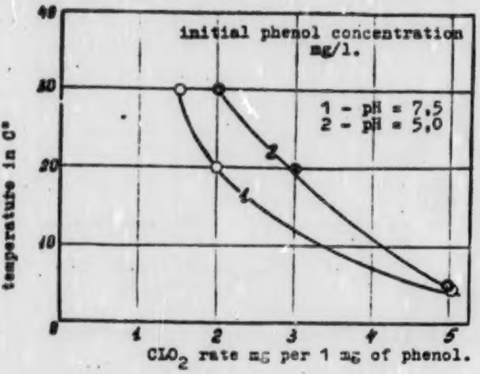


Fig.5 Effect of temperature onCLO_2 rate required for complete phenol oxidation.

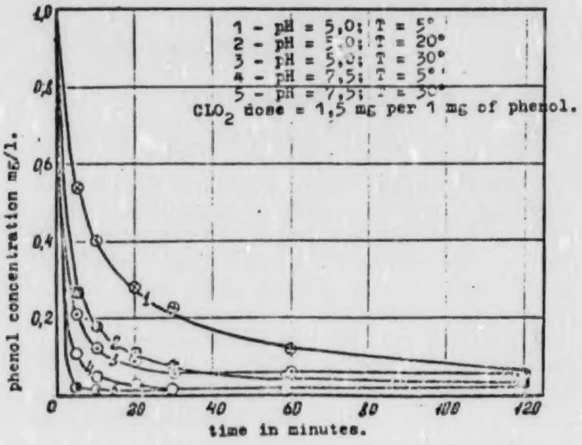


Fig.6 Effect pH value and temperature on phenol oxidation rate.

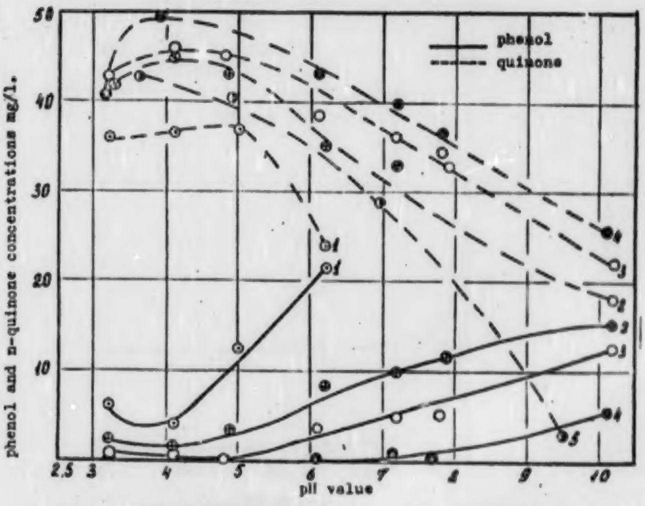


Fig.7 Effect pH value on phenol and n-benzoquinone concentrations at various ClO_2 doses.
1- 0,7 mg/mg.; 2 - 1,0 mg/mg.; 3 - 1,2 mg/mg.;
4 - 1,5 mg/mg.;
4'- 1,5;1,7 and 1,2mg/mg;
5 - 5 mg/ 1 mg phenol.

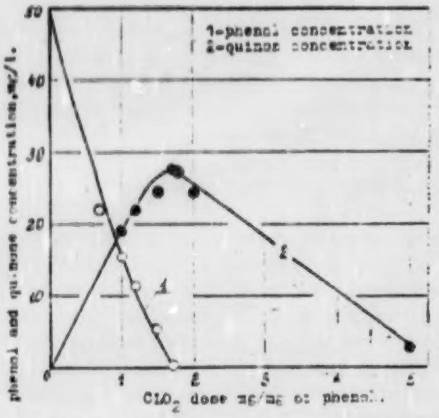
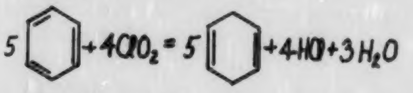


Fig.8 Phenol and n-benzoquinone concentration variations vs. [illegible] at pH = [illegible]

By using physical-chemical methods of analysis for acid fraction (on absorption spectre both in the ultraviolet and polaro-graphically) malcic acid was identified as a main product of oxidation. Oxalic acid is also identified and a group of volatile acids is isolated (acetic and formic acids are assumed to be among the acids).

During phenol oxidation chlorine dioxide is mainly reduced to chloride ions. The process may be presented by the following summarized equations:

in acid and neutral media



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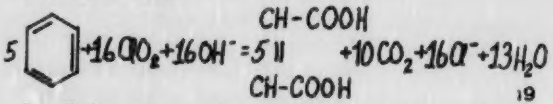
in alkaline media



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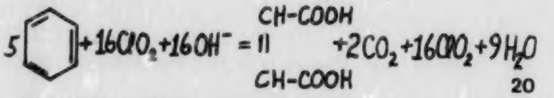
In alkaline media chlorine dioxide is partly reduced to chlorite ions as:



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Therefore chlorine dioxide rate required for oxidation of one weight part of phenol in alkaline media constitutes five weight parts that is some more of that by equation (19) (2.4 mg/mg) and it is greatly less of that by equation (2.0), therewith CLO_2 being reduced to chlorite (12mg/mg).

Cresols and multiatomic phenols (hydroquinone, resorcinol, pyrogallol, pyrocatechol) occur in addition to simple phenol (carbolic acid) in waste effluents of several industries and hence in water of streams into which the mentioned effluents are discharged.

During chlorizating process cresols similarly carbolic acid may form chloroderivatives the presence of which in water is dangerous in organoleptic respect as in the case of phenol content.

Multiatomic phenols are toxically harmful. Not so much important cited in the literature on oxidation both of cresols and multiatomic phenols either by chlorine dioxide or other oxidizing agents justify that they are more readily oxidized than carbolic acid especially in alkaline media. As a result of their oxidation the proper compounds of quinone structure assumed thereto to be formed. The data as concerns subsequent conversions of such compounds being influenced by various oxidizing agents are not complete.

We attempted to disclose the mechanisms of oxidation of cresols, quinones and multi- atomic phenols by chlorine dioxide as well as to identify the products produced during reactions.

The oxidation processes are considered on the following examples:

– cresol oxidation on that of metacresols,

– quinone oxidation on that of n-benzoquinone,

– multiatomic phenols oxidation on that of resorcinol.

The studies on metacresol oxidation showed that it is readily oxidized by chlorine dioxide. Both its oxidation efficiency and specific rate of chlorine dioxide are only a slight dependent on pH value in the 3-10 range.

The main products of reaction are quinone compounds (it is likely their methyl-derivatives). However their quantity didn't correspond to one of oxidized cresol and didn't depend on pH value. So during complete oxidation of cresol in amounts of 51 mg/l quinone compounds were determined to be 23329 mg/1., i.e. only 55-60% of cresol was oxidized to quinone.

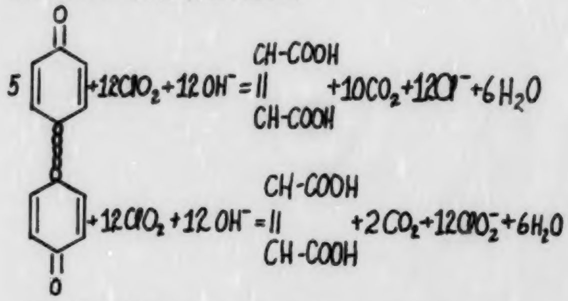
It is possible to assume that at any pH value cresol being affected by CLO_2 in addition to oxidation to methilquinone undergoes more deep destruction by forming the decomposition products of benzol zinc (for example of methylmaleic acid) that are not identified in our paper.

Chlorine dioxide rate during oxidation insignificantly raised as pH value increases (over the range from 3 to 10) and was in amounts of 1.2 - 1.3 mg/mg.

The tests on n-benzoquinone interaction with chlorine dioxide showed that inter n-benzoquinone was not oxidized by chlorine dioxide in acid and neutral media. The oxidation of n-benzoquinone effectively occurs in alkaline media (pH≈10) at chlorine dioxide rate of 3 mg per 1 mg of quinone.

N - quinone oxidation by chlorine dioxide in alkaline media was found to be followed by forming carboxylic acids among which maleic acid is the basic one.

The oxidation process may be described by the equations (21), (22), as follows



During oxidation process chlorine dioxide is reduced to chlorite and chloride ions that is confirmed by its rate (3 mg/mg i.e. twice as much of that by equation (20) (1.5 mg/mg) and 2.5 times as less of that by equation (21) (7.5 mg/mg).

On the basis of performed investigations into oxidation both carbolic acid and n-benzoquinone there may be stated that hydroquinone will be oxidized only to n-benzoquinone in acid and neutral media.

In alkaline media the process proceeds similarly to oxidation of quinone by breaking a ring and forming carboxylic acid. For this reason it was of interest to study oxidation process of other biatomic phenols interarrangement of hydroxylic groups of which proved to be either in meta or orto position rather than in para one.

The resorcinol solutions (m - dioxybenzol) were subjected to chlorine dioxide treatment. The investigation showed that oxidation intensity of resocinol insignificantly raises as pH value increases (Fig. 9). So at introducing CLO_2 in amounts of 0.5 mg per one mg. of resorcinol the last was oxidozed by 84% at pH=3; by 91% at pH=5.5; by 94% at pH=8; by 100% at pH= value in the range of 10.3-10.6. By using 2 mg of CLO_2 per 1 mg of resorcinol the last was oxidized completely at any pH value. The process occurs by forming intermediate compounds of quinone structure (OXY - para-quinone is assumed to be).

In acid media the formed intermediate compounds are simultaneously oxidized with resorcinol. In neutral acid media the last do not subject to destruction until the whole resorcinol is completely oxidized.

The process rate is enough high and the following conditions are accepted to be optimal:

- the rate of oxidizing agent is of order of 1.5-2 mg per one mg. of resorcinol,
- pH value is in 5.5 - 8 range.
- the contact time is over 20-30 minutes.

Organic acids and CO_2 are the end products of reaction. Both maleic and oxalic acids among organic ones are identified muconic acid is assumed to be present.

On the basis of carried out investigations into oxidation of n-benzoquinone and resorcinol as well as after studying the numerous researches works we can conclude:

- The oxidation process rate of diatomic phenols (and quinones) depends on the interarrangement of hydroxyl groups (and quinone grouping). The benzol ring of phenol (or proper quinone) is less subjected to breaking up under chlorine dioxide action if hydroxyl groups (or quinone grouping) are in para-position relative to each other (hydroquinone, para-bezoquinone) and they are distructed more readily when the group arrangement is reproduced either in meta position (resorcinol) or in orto position (pyrocatechol, O-quinone).

Methyl-derivatives of quinone do not undergo to destruction. Phenols having methyl substituent in side chains are oxidized only to methyl-quinone.

Having studied chlorine dioxide reaction in the presence of some specific substances we examined chlorine dioxide effect on waste effluents containing such compounds.

The biochemically treated refinery plant effluents that contained nonoxidized oily hydrocarbons and the products with various degree of their oxidation (COD is of 100-150 mg/1) were affected by chlorine dioxide effect.

The performed experiments showed that the substances retained in mentioned waste effluents being biochemically treated are oxidized only in the presence of large excess quantity of CLO_2 with maximum effect in strong alkaline media.

Removing COD by 90-95% is achieved by using chlorine dioxide rate of 800-1000 mg/1 (5 - 8 mg per 1 mg of removed COD).

Phenols that contained in refinery plant effluents being biochemically treated and in smallconcentrations (0.1-1 mg/1) are effectively oxidized by chlorine dioxide. Their complete oxidation is obtained at CLO_2 rate of 5 mg/1 over the period of 10-15 minutes.

The results of comparative tests on phenol oxidation by calcium hydrochlorite in the same effluent indicated that for achieving such effect "the activated chlorine" required to be twenty times as much (100 mg/1).

Therefore chlorine dioxide utilization holds much promise for advanced treatment of waste waters with phenols content in small concentrations.

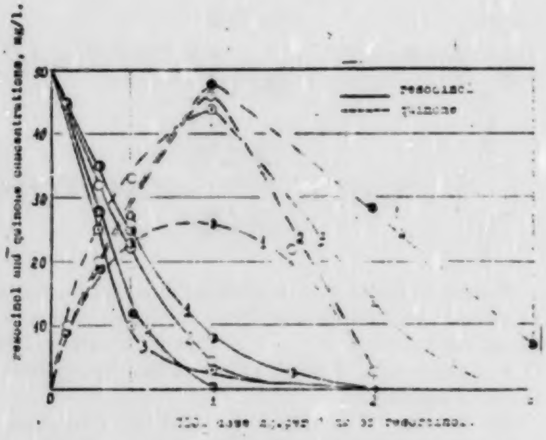


Fig.9 Resorcinol and quinone concentration variations vs. ClO_2 dose at various pH values:
1 - pH =3; 2 - pH=5.5; 3 - pH=7.2-8.0;
4 - pH=10.0 - 10.3.

CURRENT STATUS AND DIRECTIONS OF DEVELOPMENT OF PHYSICAL-CHEMICAL EFFLUENT TREATMENT IN THE PAPER INDUSTRY

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INTRODUCTION

For purposes of this discussion we feel it is desirable to advance a definition of physical-chemical treatment sufficiently broad to encompass the following approaches:

- chemical assistance to separation processes normally defined as physical, such as flotation, sedimentation, and filtration, particularly for removal of suspended materials and dewatering of a variety of sludges,
- use of chemical reactants to remove or chemically alter organic constituents of effluents whose presence is not desired in the receiving stream,
- physical treatment of specific process effluent streams to remove undesired chemical constituents, as in steam-or air-stripping of spent kraft or sulfite liquor condensates.

Viewed in these broad terms, physical-chemical treatment is seen to have had a lengthy history of attention in our industry, and therefore been the subject of changing emphasis as well. Initially it took the form of coagulant-assisted clarification of wastewater, particularly at waste paperboard mills, for enhanced removal of waste paper fines, and more highly clarified whitewater for improved in-process reuse.

More recently the emphasis has shifted toward (a) possibilities for substituting physical-chemical treatment for biological treatment as a means of meeting effluent standards in such areas as fine paper and tissue production, (b) removal of biologically refractive constituents of pulping and bleaching effluents responsible for their color, (c) enhanced dewatering of sludges high in content of hydrophilic materials, and finally (d) selective reduction of oxygen-demanding organic constituents of particular process wastes as part of an approach toward optimization of design of wastewater management systems combining physical-chemical and biological stages deployed both within and external to the manufacturing process.

The problems toward which physical-chemical treatment is being directed are therefore numerous and include the following, (a) improved effluent clarity following either primary or secondary treatment, (b) improved dewatering of sludges generated in either treatment system, (c) enhanced opportunities for wastewater reuse in papermaking through removal of suspended matter and objectionable organic constituents, (d) relief of overload conditions at biotreatment facilities, (e) decolorization of pulping and bleaching effluents to avoid receiving water discoloration or other undesired effects, (f) reduced possibilities for odor emission at biotreatment facilities, (g) improved means for processing neutral sulfite semichemical (NSSC) spent liquors at non-integrated mills, and finally (h) economic and technical optimization of wastewater management systems.

The technologies included in consideration of physical-chemical treatment are therefore also quite numerous and include (a) sedimentation, (b) flotation, (c) fine screening, (d) filtration through granular media, (e) chemical precipitation, (f) chemical oxidation, (g) activated carbon adsorption, (h) steam or air stripping, (i) ion exchange, (j) reverse osmosis and ultrafiltration, and (k) solvent extraction, and perhaps others as well.

What follows in this paper is a systematic yet necessarily brief and somewhat summary discussion of this broad range of physical-chemical treatment approaches, and finally some comments as to the directions along which their further development and application may lie.

SEPARATION OF RESIDUAL SUSPENDED SOLIDS

As suggested earlier, this approach has been pursued more extensively at non-integrated fine paper and tissue mills than at integrated chemical pulp and paper mills. This is particularly the case with regard to further clarification of excess machine white water before discharge and has included chemically-assisted flotation, pressure filtration, multimedia gravity filtration and microstraining. More recently consideration has also been given to improving the clarity of biotreated effluents from both integrated and non-integrated mills.

Clarification of Non-Biologically Treated Effluent

Flotation Clarification of Tissue Mill Effluent – One example of this approach is provided by the Scott Paper Company facility at Fort Edward, New York. Pilot-scale trails at this tissue mill led to a control installation consisting of a pressurized air flotation system followed by continuous centrifuge sludge dewatering. Chemical treatment proposed for full-scale operation included a standard cationic polyelectrolytic retention aid for flotation, alum and caustic to aid floc formation and activated silica for improved floc strength. Chemcial treatment costs were estimated in 1967 at $110,000 annually for treatment of 6 MGD. Since placing the system in operation in 1972 there have been a series of trails of various cationic polyelectrolytes, substitution of lime for caustic for flocculation pH control, and modification of the centrifuge as well. It is believed that this process is capable of removal of 85 to 90 percent of the suspended solids remaining after normal fibre recovery and 60 to 80 percent of the residual BOD.

Pressure Filtration of Fine Paper Mill Effluent – Weyerhaeuser's Miquon, Pennsylvania mill produces 250 TPD of fine printing papers using pulps delivered from other mills, and employed 12,000 gallons of water per ton at the time this control system was installed. The mill was equipped with an alum and caustic-assisted clarifier. Uncertainties regarding future water supply sources and a desire to meet expected effluent standards by means other than biological treatment prompted a program that would lead to both improved effluent quality and more extensive reuse. A pressure filter evaluation program led to a decision to employ such a filter believed capable of reducing clarifier effluent suspended solids from 0.6 lbs per 1000 gallons by 85 percent to 0.1 lbs per 1000 gallons. In actual practice, however, full-scale operation produced only 50 percent reduction, attributed to floc degradation resulting from excessive agitation of the filter feed.(1)

Further improvement has, however, been effected by addition of a starch hydrolysis enzyme prior to clarification to eliminate the turbidity and suspension-stabilizing properties of residual starch. Under these conditions filtered effluent solids have been reduced to 0.05 lbs per 1000 gallons from a clarifier influent level of 5.6 lbs per 1000 gallons. BOD reduction has, however, remained below 20 percent.

Microstrainer Clarification of Fine Papermill Effluent – Currently serving the Esleeck and Strathmore Paper Company mills at Turners Falls, Massachusetts is a microstrainer system consisting of two 10 foot diameter x 10 foot length units with 23 and 35 micron screen openings, handling 1.7 MGD. Coagulation and filtration aids now in use include an anionic polyelectrolyte at a 1 ppm dosage, and either alum or caustic for pH adjustment. Coupled with measure to (a) reduce starch usage and improve retention, and (b) tighten control over water usage, turbidity, suspended solids and BOD reduction have reached 93, 98 and 88 percent respectively. Deposition on the screens which interferes with successful operation is overcome by periodic treatment with 10 percent phosphoric acid. The sludge produced is dewatered in a nearby municipal system at a cost of $1 per ton of paper production in addition to the normal operating costs of $2.50 (1973 data) for the microstrainer system. (2) (3).

Polishing Filtration of Primary Effluent – Studies by our organization at a coated fine paper mill have shown erratic results stemming from frequent grade changes and resultant changes in effluent composition. Using polymeric addition to an alum and caustic-assisted clarifier effluent, BOD reductions during polishing remained below 40 percent while suspended solids and turbidity were reduced by 80 and 60 percent respectively. No provisions were developed for disposal of the backwashed solids and this problem still remains to be resolved. (4)

Clarification of Biologically Treated Effluent

The specifications of a small full-scale system serving a tissue mill, and the results of several pilot plant trails are summarized below.

Clarification of Tissue Mill Effluent – Ponderosa Products at Flagstaff, Arizona currently produces 40 TPD non-integrated tissue and provides 10 days aerated stabilization basin treatment followed by effluent polishing in two anthracite/sand mixed media gravity filters operated at 2 to 4 gallons/sq. ft./min. The filtrate is chlorinated and recycled to the mill as process water.

Clarification of Kraft-NSSC Cross-Recovery Mill Effluent – The Great Southern Paper Company at Cedar Springs, Georgia discharges an aerated stabilization basin effluent containing 65 ppm suspended solids. Coagulation tests indicated an alum requirement for flocculation of 70 ppm. Using multimedia filtration and no chemical treatment a reduction of 50 percent suspended solids was achieved at 2 gal/sq.ft./min with no measurable BOD reduction. Alum dosage produced no discernible benefits in either BOD or suspended solids reduction. Scaleup costs for a 20 MGD system serving a 2000 TPD mill indicated that costs for reducing suspended solids from 12.5 to 4.2 lbs per ton product would exceed $3 per ton. (5).

Polishing Filtration of Secondary Effluents – Studies by our organization using three different filtration approaches indicated modest suspended solids and BOD reduction benefits with alum and polymer additions, with the problems of filter backwash disposal still remaining to be resolved. (4)

Microstraining of Secondary Effluent – The microstaining process is currently being commercialized at an integrated bleached kraft mill practicing activated sludge treatment. The system will contain three 6 foot diam. x 8 foot units using a 21 micron polyester fabric, loaded at 1300 gal/minute/filter. Backwash flow is to consume 2 percent of the throughput. Pilot plant results indicate expected removals of 70 percent suspended solids and 30 percent BOD. (6)

Upgrading of Filtered Effluents for Process Reuse

The Weyerhaeuser, Miquon mill has also explored reuse possibilities for its pressure-filtered primary effluent. Filtrate color presents one obstacle to such reuse due to the variety of white and colored grades produced. This problem has been minimized by filtrate chlorination at a 3.5 ppm dosage rate. Slime accumulations accompanying reuse were also minimized by a special tank cleaning schedule. A major improvement in resue capability was, however, achieved by introduction of enzymes for residual starch hydrolysis as noted earlier. Currently, recycled effluent accounts for 50 percent of total daily water use.

SEPARATION OF DISSOLVED ORGANIC MATERIALS

Among the physical-chemical treatment approaches considered here are (a) condensate stripping and processing, (b) NSSC spent liquor processing and integration of reverse osmosis in the NSSC machine water system, and (c) use of activated carbon in papermill effluent systems.

Processing of Chemical Pulping Liquor Recovery Condensates

Progress has been recorded recently in this area for both kraft and sulfite liquor condensates as follows:

Kraft Condensate Processing – An early approach to condensate stripping for BOD load reduction was reported by Estridge (7) in which evaporator condensates, barometric condenser water and turpentine decanter underflow at an 850 ton per day linerboard mill were recycled to a cooling tower. Aeration of these process streams in this manner achieved a load reduction of 10,000 lbs BOD per day due almost exclusively to air stripping of methanol and other volatiles. An inherent drawback lay, however, in the transfer of odorous volatiles such as terpenes and organic sulfides to the atmosphere.

This deficiency has been met by systems employing either air or steam stripping with the stripped material being burned at a subsequent combustion unit. An example of such a system is that in operation at the Mead Corporation mill at Escanaba, Michigan. Initially this 800 ton bleached kraft mill installed a steam stripper handling hot water accumulator overflow, turpentine decanter overflow, evaporator condensates and miscellaneous hot odorous streams. The initial objective was to reduce odor release at the biotreatment system. This was accomplished using a fractional distillation column 53 feet high containing 24 trays, and steamed at a 2.5 percent rate, with non-condensibles and collected foul air burned in the lime kiln (8).

In 1973 a program was begun to determine whether the mill BOD load could be significantly reduced as well. Analysis showed that the stripper bottoms contained 15 to 18,000 lbs BOD daily and that 90 percent of this was accounted for by the methanol present in the condensates. Modifications to the system enabled the steam feed to be increased to 8 percent so that the residual BOD was reduced to 4 to 5,000 lbs daily for a net reduction of 11 to 13,000 lbs daily. Total steam and power requirements are reported as 8000 lbs/hr of 60 psi steam and 65 HP for pumping condensates.

Sulfite Condensate Processing – Currently underway at the Flambeau Paper Company, Park Falls, Wisconsin sulfite mill is a project directed toward demonstrating the possibilities for recovering methanol, furfural and acetic acid as ethyl acetate from sulfate liquor evaporation condensates. The process being investigated involves steam stripping and activated carbon adsorption to achieve removal and separation of these components. This investigation expands on a project previously conducted at the Institute of Paper Chemistry. (9)

Another physical-chemical treatment approach pertinent to sulfite liquor condensates involves the upward adjustment of spent liquor pH prior to evaporation so as to retain the volatile acids in the liquor concentrate, permitting their destruction in the liquor furnace, rather than allowing their entry into the condensates. Previous studies have shown that upward adjustment of liquor pH from 2.5 to 4.0 could result in condensate BOD load reduction from 150 to 200 lbs per ton to 50 lbs per ton. (10).

Processing of NSSC Spent Liquor and Excess Machine Water

Spent Liquor Processing – Sonoco Products, Inc. at Hartsville, S.C. recently has patented and commercialized a novel process which facilitates the incineration of, and subsequent chemical recovery from its spent sodium-base NSSC liquor. Essentially, the NSSC liquor is concentrated in multiple effect evaporators to 40 to 50 percent solids and mixed with finely divided reactive alumina hydrate to form sodium aluminate which results in solidification of the liquor concentrate. A rotary pelletizer converts the solidified liquor to small pellets with desirable incineration properties. First, a reducing atmosphere is maintained within the pellet, leading ultimately to formation of sodium aluminate and SO_2. Second, elevated temperature burning is possible at 1800°F. The ash is dissolved and used to scrub the SO_2, thereby releasing a hydrated alumina cake for recycle and producing sodium sulfite solution for use in new NSSC cook liquor. (11)

Processing of Excess NSSC Machine Water – Green Bay Packaging Company at Green Bay, Wisconsin has made a novel installation of reverse osmosis technology designed to assist the operation of a high dissolved solids machine water system. Excess water is bled out of the system through a small 20 gpm reverse osmosis unit containing 300 separation modules, and is used as fresh water for pump seals. This has assisted in reducing mill BOD load to less than 10 lbs per ton product. (12)

Removal of Organic Materials from Paper Mill Effluents Using Activated Carbon

Explorations of activated carbon treatment have been undertaken at a number of non-integrated paper mills involving in several instances combined treatment with municipal sewage. Included among these are (a) St. Regis, Bucksport, Maine, (b) Fitchburg Papers, Fitchburg, Massachusetts, (c) Mohawk Papers, Waterford, New York and (d) Neenah, Menasha, Wisconsin. Details of several such projects are as follows:

Fitchburg, Mass. – Pilot studies for a full scale project involving 14 MGD from two paper mills and 1.25 MGD municipal effluent were conducted using a process consisting of chemical coagulation with alum, sedimentation and activated carbon column treatment. Process results indicated an anticipated 50 percent BOD reduction through coagulation, followed by 82 and 86 percent reduction in COD and BOD passing through four carbon columns at 3.4 gal/sq. ft./min. The activated carbon process design criteria selected were 7.2 lbs carbon/lb BOD at exhaustion, 30 minutes contact time, and reactivation in a multiple hearth furnace. Costs were estimated at $2.1 million for construction of the carbon system in 1970, and $140,000 for annual operation, of which 70 percent is carbon makeup. The facility has been constructed, but operating results are not yet available. (13)

Neenah – Menasha, Wisconsin – A pilot plant study was performed using municipal sewage containing 80 percent paper mill effluent. The process studied involved chemical coagulation with ferric chloride, sedimentation, high rate filtration at 12 gal/sq. ft/min. to remove fibrous material followed by a second filtration stage at 9 gal/sq. ft/min through PVC media, and upflow expanded bed filtration through 14-40 mesh carbon at 3 to 5 gal/sq. ft./min. Results obtained by the IPC study group indicated removals of BOD, COD and suspended solids prior to carbon treatment of 76, 83 and 98 percent respectively. Following carbon treatment, overall reductions were increased to 93, 95 and 99.5 percent respectively. Project costs were estimated in 1973 at 17 cents per 1000 gal capital and 35 cents per 1000 gal operating for a total of 52 cents per 1000 gal for a 10 MGD plant. (14)

DECOLORIZATION OF KRAFT PULPING AND BLEACHING EFFLUENTS

Basic Elements of Effluent Decolorization Problem Definition

Measurement of Effluent and Receiving Water Color Levels – Selection of methods for measurement of pulping– and bleaching– derived color has always proceeded from the observed similarity in hue between so-called natural water color of swamp or decaying vegetation origin and that of mill effluents. Starting with color wheel visual comparators we have evolved most recently to single wavelength spectrophotometric measurements in the spectral range of 450 to 480 mu where both effluents and the cobalt-chloroplatinate standard display flat adsorption curves.

The procedure most recently found useful (15) involves pH adjustment to 7.6 followed by filtration through an 0.8 micron porosity membrane filter so as to produce a high clarity sample without significant removal of non-filterable color. Color is then determined by light absorption measurement at 465 mu and expressed in standard color units read against a calibration curve prepared with the above standard. While this procedure is not as yet incorporated in *Standard Methods* it has been recognized by EPA in its proposed effluent color standards.

Detectible Changes in Receiving Water Color – One major problem definition deficiency continues to exist in the most important area of all, namely a determination of the variability in level of color detectibility in different receiving waters, and at different points along or overlooking such waters. We have recently completed a pioneering investigation of this problem. These studies have employed professionally screened observer panels to determine (a) absolute thresholds of detectible color level, (b) perceptible changes from a given visually observable reference color level, and (c) the influence of lighting conditions, water depth and quality, and observer angle. The importance of such information in establishing rational water quality standards and ultimately defining the goals of decolorization technology research is seemingly obvious, yet such work has not bee previously reported.

Adverse or Beneficial Effects of Receiving Water Color – Aside from human objection to receiving water discoloration on aesthetic grounds, little of substance has been heard concerning other adverse effects. Occasional comments are made concerning possible interference with light energy penetration for support of photosynthetic primary productivity processes, yet no evidence is presented to this effect. On the contrary, our own aquatic biology productivity work using high concentrations of biotreated colored effluents indicate the absence of effects above color levels that would probably be detected by humans. Downstream water supply treatment problems receive only isolated mention as a basis for setting decolorization requirements.

Inventory of Mill Process Color Loads and Sources – Color load inventories are proceeding actively at selected mills where decolorization needs have already been identified as a consequence of inadequate receiving water dilution. Often these reflect application of some control measures, and do not therefore provide necessary broad background information. We have recently completed a field survey of both bleached and unbleached chemical pulp mills, supplemented by determination of the color contribution potential of numerous spent pulping liquors, since these are the major source of pulp mill color load. Preliminary findings for kraft mills indicate a color equivalency of 2 lbs of color units per lb of hardwood liquor solids, and 1.2 lbs for softwood liquors. On a mill-wide basis the average pulp mill color load appears to fall between 100 and 200 lbs per ton. With regard to the bleach plant itself, the survey indicates that the first two stages (chlorination and caustic extraction) account for 200 lbs color per ton at hardwood mills, while in softwood operations the load is 350 lbs.

Chemical Precipitation Processes for Effluent Decolorization

General Basis for Precipitation Processes and their Current Variants – The principal approach to chemical precipitation has involved use of lime for that purpose. More recently magnesium oxide has received attention for NSSC effluent decolorization, while alum has recently found application for kraft effluent. As determined by fundamental investigation at the New York State College of Forestry at Syracuse University (16) (17) the metal ion precipitation processes are all dependent on the relatively low solubility of the metallic salts of the colored weak organic acids.

A number of mill-scale variations on the lime precipitation process have evolved in the last fifteen years including:

- The massive lime process involving slaking of reburned lime in caustic extract followed by re-solution of the precipitated color in the recausticizing process and ultimately burning of the colored organics in the recovery furnace,
- addition of minimal lime dosages to total unbleached kraft effluent in the primary clarifier, precipitating the color and dewatering the sludge in admixture with the lime mud, and burning the color in the lime kiln,
- precipitation of colored substances in the caustic extract or other specific colored effluents using minimal amounts of lime slurry followed by dewatering in admixture with lime mud and burning of the colored organics in the lime kiln, or use of lime mud, fortified with additional reburned lime or hydrate, to precipitate color and again destruction in the kiln.

Massive Lime Treatment – This process received large-scale studies at International Paper's Springhill, Louisiana mill from 1970 to 1971 and was found to remove over 90 percent of the caustic extract and unbleached decker effluent, or about 60 to 70 percent the process color load. A dosage of 20,000 ppm lime produced a sludge settleable to 18 to 22 percent solids and filterable to 50 percent for subsequent recausticizing use. The demonstration plant was rated at 530 gpm flow. An ability to produce a 740 color unit effluent was demonstrated using the entire lime kiln output to treat one-seventh of the mill flow. Costs were found to approximate $1.80 per ton of bleached pulp. While the reuse of white liquor was not affected, needs for expansion of pulping liquor preparation and recovery were identified. These have included (a) 15 to 20 percent additional capacity for green liquor slaking and causticizing, white liquor clarification and lime mud washing, and (b) 2 to 8 percent increases in pulp washing, black liquor evaporation, recovery furnace and accessories, and lime mud filtration and lime kiln facilities. (18)

Since completion of the EPA contract mentioned above, the demonstration facilities have been operated using the lime mud modification with sweetener lime added as needed to meet stoichiometric lime requirements. Both caustic extract and pulp mill decker effluent have been studied with apparent success as regards effluent decolorization and quality of the reburned lime, although caustic extract alone appears to be more readily decolorized using the massive lime alternative.

Lime Precipitation of Color During Primary Clarification – The first trial of this decolorization approach was undertaken by Interstate Paper Company with EPA support at the Riceboro, Georgia unbleached kraft linerboard mill in 1968. Initial state permit requirements for discharge to an extremely low flow estuary allowed a color level of 30 units, so as to prevent excessive discharge of slowly degradable lignin-derived organic matter that would remain unoxidized during biotreatment.

A lime precipitation process was installed at the primary clarifier of this initially 4000 TPD mill at a $451,000 cost. A dosage of 1000 ppm lime reduced the color level from 1200 units to as little as 125 units. The resultant sludge was sent to lagoon storage. Recarbonation trials have shown that 20 minutes residence time and lime kiln stack gas reduces residual lime from 750 ppm to 120 ppm. During these trials recarbonation occured naturally in a large nonaerated biooxidation basin. Here some color reversion ocurred, probably as a result of alkaline extraction from the lagoon bottom. Costs were estimated at $2 per ton total. (19)

The Continental Can Company, Hodge, Louisiana mill recently completed work on an EPA-supported contract involving full-scale demonstration of yet another patented lime process modification (20) (21). The process involves use of low lime dosages at the point of primary clarification of unbleached kraft and NSSC boardmill effluents, followed by solid bowl centrifugation and calcining in the lime kiln for both fibrous sludge disposal and lime recovery. The decolorized effluent is recarbonated and clarified again with the additional sludge dewatered on the lime mud vacuum filter before calcining. Color reduction averaged 80 percent during periods of no NSSC production, and at least 15 percent less with NSSC pulping operations. The process is believed capable of over 90 percent decolorization when operating on kraft alone. Operating costs alone were estimated at 50¢ per ton of pulp for this mill when operated at 1500 TPD and 13 MGD total flow to treatment.

A question arose regarding the tendency of lime-decolorized effluent color to rise during residence in earthen storage or aeration basins. It was believed that this resulted from an alkaline extraction of organic matter from the basin waslls and bottom, and could therefore be controlled by pH adjustment where necessary. Recent EPA studies (22) have confirmed that the colored material reappearing in the basin contents is spectrally identical with that of organic matter present in nearby marsh waters. Further, lime solutions were in fact found capable of leaching color from mud samples taken from the basin bottom.

Minimal Lime Decolorization – Also having received study at two Georgia-Pacific bleached kraft mills at Woodland, Maine and Crossett, Arkansas is yet another patented lime process modification. Issued to M. Gould (23) the process as employed at the mill recycles highly colored caustic extract through the wood room, following which slaked lime is added to precipitate color. Sedimentation of wood and bark fibres and color sludge is accomplished and the resultant sludge is dewatered by special blending with the lime mud before filtration. The combined filter cake is then calcined for lime recovery and organic matter destruction.

Alum Precipitation – Alum treatment received early investigation since it had been shown capable of decolorizing potable water supplies, but commercialization was hindered by sludge dewatering problems. More recently Fuller at Gulf States Paper Corporation has patented a process (24) for alum precipitation of effluent color after secondary treatment, in the presence of alum mud. Thickened sludge is blended with primary and secondary sludges and dewatered to 30 to 40 percent solids in pressure filters before incineration in a multiple hearth furnace. Recovery of alum for reuse is accomplished through acidification with sulfuric acid. The facility has only recently been placed in operation, and is planned to achieve over 90 percent decolorization. Possible reuse of the treated effluent is being considered. Alum mud from a nearby alum plant served as the initial alum source.

Activated Carbon Decolorization

NCASI Investigations – The basic possibilities for using activated carbon to achieve high efficiency color removal from kraft effluents were first indicated by Berger (25) and McGlasson (26) (27). Their investigations showed that extensive decolorization, up to 99 percent and with residual levels as low as 10 color units, could be achieved, but at a cost significantly greater than previously estimated for the lime precipitation process. A two-stage lime and activated carbon process was put forward capable of achieving extremely low residual color levels.

The variables affecting carbon adsorption were examined for process optimization. The transport mechanism was determined and the carbon particle size was found to have the greatest effect on color removal. Internal diffusion within the carbon particle was found to be the controlling resistance. A maximum adsorption of 10 percent by weight was found obtainable under optimum conditions.

St. Regis Investigative Program – More recently St. Regis Paper Company, with partial EPA support, has been engaged in a program for the development of an economical system for maximum water reuse in the unbleached kraft pulp industry for both pollution control and water conservation. The program has been based on two principal concepts, (1) activated carbon effluent treatment, and (2) on-site production of activated carbon from kraft black liquor by a proprietory pyrolysis process with subsequent burning of the exhausted carbon for energy capture.

Results are now available from a four-year pilot plant program in which staged treatment involving (1) primary clarification, (2) biooxidation, (3) lime treatment, and (4) carbon adsorption was studied in various configurations. Starting with effluent containing 1000 color units, 250 ppm TOC and BOD, reusable water containing 100 ppm TOC and 100 color units could be produced. The most economical process was found to involve low lime additions followed by carbon adsorption in downflow granular carbon beds.

Capital costs for 10 MGD from an 800 TPD mill was estimated in 1974 at $7 million, with predicted operating costs of 30¢ per 1000 gallon or $3.50 per ton production, including credit for the reused water. Carbon adsorption in continuous countercurrent stirred contactors was also believed to have promise of lower operating costs and substantially lower capital costs.

Decolorization Using Resin Separation Processes

The resin separation approaches which have been considered include (a) reverse osmosis membrane separation, (b) ultrafiltration, (c) ion exchange, and (d) granular resin separation through non-ion exchange processes. Dynamically formed membranes are also currently under study.

Reverse Osmosis Membrane Separation – The results of an extensive laboratory and field study in reverse osmosis processing of a number of pulp and paper waste streams were reported in 1972 by Wiley et al. (19) (20) Color rejection from kraft caustic bleach effluent was in excess of 99 percent at inlet pressures of 500 psi at 35°C, using cellulose acetate membranes. Optimum performance was achieved when concentrating the dilute feed by a factor of about 10 for further separate processing and chemical recovery of the concentrate.

It was, however, not possible to demonstrate sustained, long-term process operating feasibility in the extended life performance tests of the membrane equipment available for these studies because of the low levels of reliability of available membrane equipment. A tentative cost estimate of $0.82 per 1000 gal. of product water produced from caustic bleach effluent was reported. Process costs appear quite sensitive to membrane module replacement and maintenance charges, to membrane permeation rates, and to increases in osmotic pressure as concentration increases. Membrane fouling due to material buildup on the membrane surface is also cited as responsible for permeate yield rate decrease, and may therefore require extensive pretreatment or cross-flow application at high velocities.

Ultrafiltration – Reduction of color in pulp mill effluents by ultrafiltration has been examined by Champion International Corporation with partial assistance form EPA with a 10,000 gallon per day (gpd) pilot plant. This approach was justified on the basis that the colored materials are of high molecular weight (> 1000). Treated streams included decker effluents and pine bleachery caustic extraction filtrate, which together comprise about 80 percent of the color from a bleached kraft mill. The pilot plant consisted of a five-stage circular wound cellulose acetate membrane unit. High color removal (90 to 97 percent) was demonstrated when operating at water recovery ratios of 98.5 to 99 percent. Pilot plant capacity (membrane flux) was 15 to 20 gal/day/ft^2 when operation proceeded smoothly. However, plugging of the membrane cartridges by residual particulates (even after precoat filtration) was troublesome.

Several prefiltration, concentrate disposal, and water reuse alternatives were evaluated.

Full-scale plant designs, and approximate capital and operating costs were estimated for systems of 1 and 2 MGD capacity. Capital costs were projected at about $700,000 for a 1 MGD plant, and $1,200,000 for a 2 MGD plant. Corresponding operating costs were projected at about 45¢/1000 gal (1 MGD) and 38¢/1000 gal (2 MGD).

Additional pilot plant tests were recommended to arrive at long-term solutions to the particulate problem and membrane cartridge life.

Granular Resin Separation – This approach has been put forward by Rohm and Haas, employing special polymeric adsorbent Amberlite XAD-8, a highly cross-linked 20 to 60 mesh resin possessing no ion exchange properties (30). The process functions best at pH 2 to 2.5 so that mixing of acid and alkaline bleaching effluents proves favorable. Higher decolorization efficiency is noted for hardwood than for softwood effluent (from 75 to 85 percent for softwood andd 85 to 92 percent for hardwood). It is claimed that adequate protection against resin fouling is provided by hydrosieve filtration and that resin life of at least five years can be expected. Resin regeneration is effected using weak wash which then transfers the colored components to the green liquor in the smelt dissolving tank. Alternatively white liquor is proposed for regeneration. While cost estimates have already been advanced for the process, it is currently undergoing extensive continuous flow small-scale pilot trials at a number of kraft mills. It is felt that more precise cost and performance data will result from these trials. Present claims for an 800 TPD bleach plant are $900,000 capital cost and $0.65 per ton operating cost. Chloride accumulation is not held to be sufficient to produce pulping and recovery system problems.

Ion Exchange – The first systematic study was conducted by Sanks (31) who screened the performance characteristics of 20 resins. In numerous cases the resins were found capable of decolorizing combined bleach plant effluent, but unable to withstand oxidative deterioration caused by exposure to individual effluents from chlorine, hypochlorite or chlorine dioxide stages. Single stage ion exchange with starvation regeneration produced water adequate for unbleached pulping while two stage desalination produced water usable for bleached pulps.

More recently both Rohm and Haas and Dow (32) have proposed resins capable of ion exchange removal of color in a broad pH range from 2 to 9. These are believed regenerable with process streams such as weak wash for alkaline removal of the exchanged colored weak acids and low color acidic bleach plant effluent for reacidification of the resin. Both processes await larger scale evaluation to determine chemical regenerant requirements and their ease of recycle back into the various mill chemical systems.

Oxidative Treatment – Finally, mention should be made of the possibilities for decolorization of effluents by exposure to ozone, chlorine, and radiation sources in the presence of oxygen.

Recent NCASI laboratory trials (33) have demonstrated the capability of ozone for decolorizing a variety of mill effluent color sources. These have included hardwood and softwood black liquors, caustic extracts, and lime decolorized simulated pulp mill effluents. Color removal: ozone usage ratios ranged from 1:3 for the latter to 5:1 for the former. For caustic extract the ratio reached as high as 20:1. The costs of producing ozone being what they are, results to date offer little encouragement concerning commercialization of ozone decolorization.

An example of the chlorination approach lies in limited use at perhaps five to ten mills and involves substitution of a hypochlorite stage for the conventional caustic extraction stage. Since the latter contributes at least 75 to 80 percent of the bleach plant color load, its elimination can result in major load reduction. The process change does not appear to be universally applicable and results in substantial chemical cost increments. Most recently investigators at Hooker Chemical have proposed this modification as an "antipollution," or APS, sequence yielding a 62 to 82 percent color reduction. The change involves using large amounts of chlorine dioxide immediately before the chlorination stage in addition to substitution of sodium hypochlorite for the caustic extraction stage (34).

A preliminary investigation of radiation-enhanced oxidation of pulpmill effluents for color reduction has been completed under our sponsorship at the Oak Ridge National Laboratory (35). The results indicate that exposure to 10^7 Roentgens in the presence of 500 psi oxygen can achieve 90 percent decolorization.

DEWATERING OF HYDROUS SLUDGES

Sludges of a hydrous nature are being encountered with increasing frequency as a consequence of (a) improved capture of long-fibre sludge components, (b) generation of excess biological cell material sludges in activated sludge treatment, (c) production of organic sludges during lime and alum-assisted coagulation or precipitation of fibre fines and colored materials, respecively. Polymer-assisted dewatering of such sludges is receiving increased attention, as are efforts to improve their dewatering characteristics through changes in physical state (freezing and thawing, and pressurized steam treatment).

More recently interest has been renewed in solvent addition processes capable of separating water from such sludges, followed by distillation of the solvent from the aqueous phase for reuse, as well as its recovery from the sludge as it is subsequently dried. Triethylamine is currently receiving consideration for this purpose.

SUMMARY – DEVELOPMENTAL TRENDS AND POSSIBLE AREAS FOR COOPERATIVE STUDY

It should be evident from this necessarily brief review of physical-chemical treatment applications and possibilities that they cover a wide range of approaches, objectives and technologies. While such treatment is only beginning to gain a position in the spectrum of control technologies in actual use, the possibilities are encouraging for their further development. This stems from four basic considerations, as follows:

(1) The need for development of more efficient control systems to match the continued growth in size and complexity of pulp and paper manufacturing facilities at locations presenting substantial water quality protection problems.

(2) The need for new control technologies capable of removing effluent constituents that are only minimally influenced by the more conventional sedimentation-biotreatment technology, such as effluent color, and possibly foam generation.

(3) The desire to assemble optimized waste water management systems combining a variety of control technologies so as to assure their most cost effective and dependable operation.

(4) The desire to increase opportunities for reuse of treated process wastewater both for water conservation purposes and to minimize discharge.

Some of the areas that suggest themselves for possible cooperative study include the following:

(1) Determination of water quality needs for both pulp and paper manufacture as a guide to development of specific effluent treatment objectives – hence identifying further physical-chemical treatment possibilities.

(2) Development of standardized test procedures for evaluation of polymeric or other chemical aids to the dewatering of sludges and the clarification of effluents.

(3) Examination of the effectiveness of various inprocess streams for regeneration of resin systems used for decolorization, as well as activated carbon.

(4) Examination of chemical recovery steps available for achieving reuse of calcium and aluminum cations for precipitation of colored effluent components.

Finally, common attention might be given to an examination of those environmental quality problems confronting our industry which our limited experience in physical-chemical treatment leads us to believe should be addressed by such technology in proper combination with the more widespread sedimentation-biotreatment technology.

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(32) Chamberlin, T.A. *etal.* "Color Removal From Bleached Kraft Effluents," Proc. 1975 TAPPI Environmental Conference

(33) "Preliminary Laboratory Studies of the Decolorization and Bactericidal Properties of Ozone in Pulp and Paper Mill Effluents," NCASI Technical Bulletin No. 269 (January 1974)

(34) Lowe, K.E., "Bleaching at Crossroads," *Pulp & Paper* p. 88 (August 1973)

(35) "A Preliminary Investigation of Radiation and Enhanced Oxidation of Pulp Mill Effluents for Color Reduction," NCASI Technical Bulletin No. 271 (February 1974)

TREATMENT OF CONCENTRATED WASTE WATERS CONTAINING OIL EMULSIONS.

by V.G. Ponomarev and S.B. Zakharina All-Union
Scientific-Research Institute VODGEO.

For metal cutting in mechanical shops special cutting oils and coolants are used representing stable emulsions with the mineral oil content up to 50 g/1.

For the preparation of such coolants cutting emulsions are used, defined as concentrated emulsions of mineral oil and emulsifying agents of the type "water in oil". Various organic matters can be used as emulsifying agents. When cutting emulsions are mixed with water, phase reversel takes place and "oil in water" emulsion generates spontaneously. Cutting emulsion content in the emulsion generated is equal to 5-10 per cent. Sometimes soda is introduced into it in quantity of 0.03%, pH of the emulsions used varies from 7 to 10.

An Analysis of the emulsion content in the process of its use at the machine-building plant has revealed that during its service-life all its components are present in it in proportional quantities. Any significant changes in oil and emulsifying agents contents or in the alkalinity are not observed.

Despite high resistance to degradation, service life of emulsions averages about a month, after this they are renewed.

Increase in the coolant's viscosity as a result of the liquid phase evaporation serves as one of the reasons for its service life reduction. To prevent it water is periodically added to the coolant.

In the process of its use the coolant is polluted by mechanical impurities, the main part of which consists of metal particles and of grinding materials. These admixtures concentration is constantly increasing, which can make the further use of the emulsion impossible. In order to prolong its service life the waste emulsion should be subjected to mechanical treatment. At the Soviet enterprises waste emulsion before its return for reuse is usually fed to installations for mechanical treatment, such as settling tanks, magnetic separators and filters manufactured from different materials.

Coolant's decay as a result of the anaeobic micro flora of sulphate-reducing bacteria growth in it is the third reason for the coolant service life reduction. Bacteria reduce sulphate present in the emulsion to hydrogen sulphide.

To prevent emulsion decay in the course of its service it is recommended to blow it off by air, thus creating aerobic conditions and preventing anaerobic bacteria growth.

Blowing off is recommended to carry out in collecting reservoires installed near the lathes, so compressed air should be fed to the lathes.

At the enterprises in operation where construction of air conduits is not possible, for decay prevention bactericidal matters such as hexachlorophen are added to the emulsion in quantity of 0.02% of the emulsion volume. As analyses showed, addition of hexachlorophen prolongs service life of the emulsion up to 4 months.

Based on the bench-scale and industrial tests a general technological scheme of an installation for waste emulsion regeneration was developed (Fig. I). According to this scheme polluted emulsion is fed to the setting tank (I), where suspended matter and oil are separated. Floated oil is fed to the oil collector (5), and suspended matter collected in the conic part is introduced to the sludge-holding tank (4). Treatment of emulsion from fine suspended solids is conducted on filters (2). After being treated on filters the emulsion is pumped over to the settling-reacting tank (3) to which if necessary and if there is odour of hydrogen sulphide 15 mg/l of KM_nO_4, I g/l of sodium nitrate and 0.2 g/1 of hexachlorophen in the alkali solution are added. Besides, to renew emulsion properties cutting emulsion and water are to be added to it. After all components were added to the emulsion, it is mixed with the compressed air, then settled to remove non-emulsified oil and then is fed to the shop. Oil isolated in the settling-reacting tank is pumped over to the oil collector (5) and then is fed to regeneration. Sludge from the sludge-holding tank is fed to the filter presses for dehydration (6).

Technical-economic evaluation of the suggested emulsion regeneration scheme shows that regeneration of I0 m^3/day of the emulsion will permit to save about 21000 rubles per year.

It waste emulsions can not regenerate, they should be decontaminated at the installations for their breaking.

While emulsions are settling within I-3 months oil concentration in them decreases only by I0-20 per cent. Due to high stability of emulsive waste waters they should be treated with the use of such chemical-physical methods as coagulation, pressure flotation with the addition of reagents and centrifugation.

In the emulsion coagulation analyses ferric salts, salts of aluminium, calcium, magnesium, which at hydrolysis give positively charged colloids of hydroxides, were used as reagents. At their interaction with the negatively charged micelles of the emulsion mutual coagulation takes place with the formation of suspensions, containing particles of metal hydroxides, sorbing at their surfaces drops of oil and of emulsifying agents.

Application of ferric sulfate with the addition of lime, ferric chlorate with sulfuric acid and aluminium sulfate with lime or sodium hydrate have appeared to be the most effective for emulsion breaking. Dosage of coagulants varies within the range of 3-7 g/1 depending on the emulsified oil content.

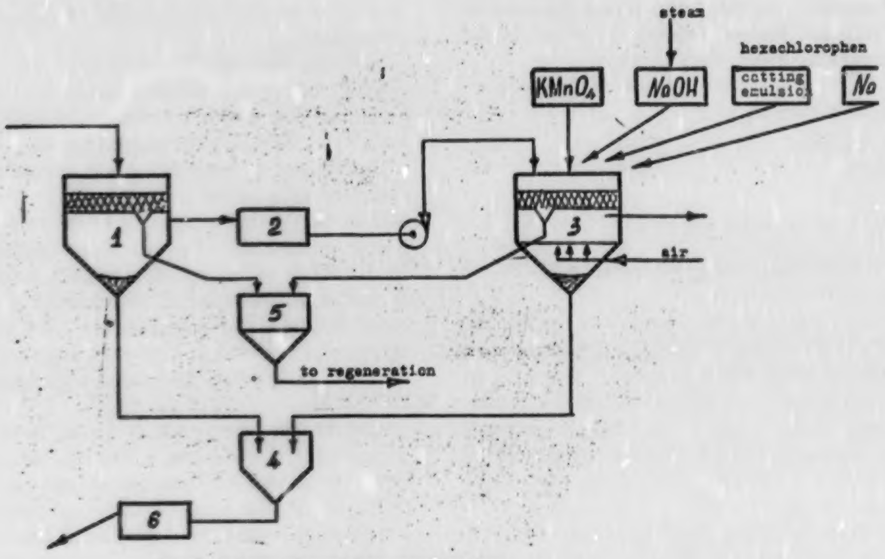
steam
hexachlorophen
KMnO4
NaOH
cutting emulsion
Na
1
2
3
air
5
to regeneration
4
6

Fig.I Scheme of emulsion regeneration

As analyses indicated, the volume of the sludge separated averages 17-20 per cent of the total effluent. Depending on the oil concentration the sludge can take different positions in the settling tank, that is to settle to the bottom of the tank, or to float to the surface. In a number of cases the sludge formed is located in the form of flocs along the whole volume of the settling tank. That is why the determination of the method for sludge separation from the waste emulsion is one of the important problems.

The method of pressure flotation with the application of reagents was investigated, and the investigations showed that this method is possible to be applied for the purpose in view. It was discovered at the pilot plant that saturation of the emulsion with the air should be conducted at the pressure of 3 atm., and the saturation

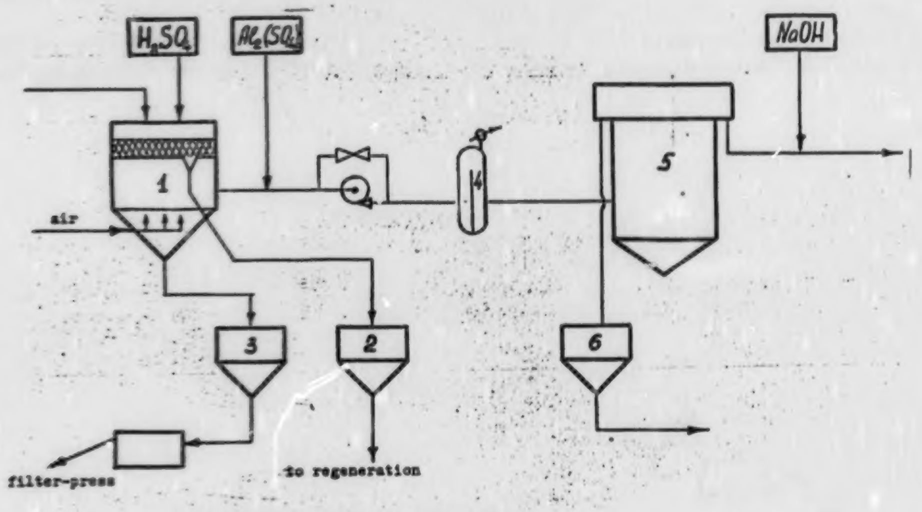
H2SO4
Al2(SO4)3
NaOH
1
air
4
5
3
2
6
filter-press
to regeneration

Fig.2 Scheme of emulsion breaking by flotation

duration is 5 minutes and the flotation period should be about 15-20 minutes. Reagents should be added to the emulsion immediately before the saturator.

Optimum doses of coagulating agents at the emulsion oil content of 30 g/l are equal to:

aluminium sulfate	6 g/l
ferrous sulfate	7 g/l
ferrous chloride	4 g/l
with addition of sulfuric acid	6 g/l

The volume of the foam formed is equal to 20-25% of the effluent being treated volume.

The content of ether soluble matters in the treated waste is equal to 0.15 - 0.3 g/l. The analysis showed that mineral oil concentration was equal to 50-70 mg/l, and the residual ether soluble matters are emulsifying agents.

With the aim of the foam volume decrease in view, tests were carried out with the Soviet flocculating agents available, such as the "Komet" flocculating agent and polyacrylamide. It was established that at these flocculating agents dose of 10-100 mg/l the foam volume is possible to be decreased by 30-50%. "The Komet" flocculating agent has appeared to be the most effective.

As a result of the investigations in the centrifugal field ability for waste emulsion degradation it was established that emulsions were broken at separation factor of 7500, centrifugation period being equal to 15-60 minutes and depends on the emulsion composition. Before centrifugation the emulsion should be treated by sulfuric acid to reach minimum pH value, taking into consideration corrosive properties of the metal, the centrifuge is made of (Fig. 3).

Being acidified to pH = 7 emulsions are broken by 60-80%. Several types of the emulsions used may be broken in the centrifugal field by 90-98% at their acidification up to pH = 3.

Centrifugation may be used as an independent method for emulsive effluent treatment when acid-proof equipment is available. Final treatment of the effluent may be conducted jointly with the total effluent of the enterprise.

On the basis of the investigations carried out, a scheme of the full-scale installation for waste oil emulsions degradation was developed which is now being built at several industrial plants (Fig. 2).

According to this scheme waste emulsion is directed from the shop to the settling tank (I) to which sulfuric acid is fed. Mixing with the acid is carried on by means of compressed air. Thus pH of the emulsion is reduced to 6-7. After waste emulsion was settled during an hour floated oil is fed to the oil collector (2), and the sludge is introduced to the sludge-holing tank (3). Emulsion, which was not broken in the settling tank is fed to the flotation unit, where the second stage of its treatment is carried on.

Coagulating agent, which is fed from the dose, is mixed with the effluent before the saturator (4). The saturator should be designed in such a way, that all discharge of the emulsive effluent passes through it. Emulsion saturated with the air is introduced to the flotation compartment (5). The condensed foam is skimmed off the surface of the flotation compartment and is fed to the foam collector (6). Clarified liquid is neutralized by means of NaOh, water or lime to pH = 7, and then is discharged to the sewerage system where it is mixed with the waste waters from the enterprises and goes to the treatment facilities of the plant for the full-scale treatment.

Foam from the flocculation unit is fed to the burners for incineration or is mixed with the sludge separated from the total effluent of the enterprise to be treated jointly.

Technical-economic evaluation of the scheme considered has shown that the cost of the oil and emulsion bearing effluent by physical-chemical methods is 60-70 copecks/m^3.

Hyperfiltration as one of the methods may be recommended for the use at the enterprises discharging

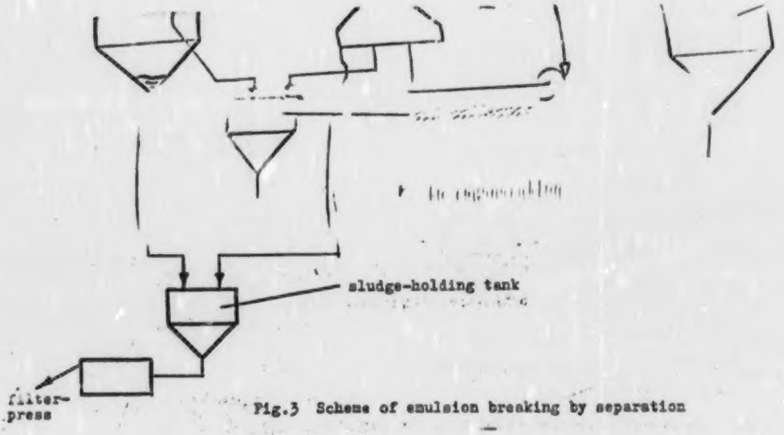

Fig.3 Scheme of emulsion breaking by separation

small amounts of emulsive effluents, in order of I-5 m^3/day.

Preliminary investigations show that at the initial oil concentration of 30-40 g/l concentration up to 350 g/l is reached without any decrease of membrane productivity; oil content in the treated water is 7-8 mg/l at the membrane selectivity of 75-80% by sodium chloride. Further concentration may lead to a slip of contaminations.

Researches on this method to be used for oil and emulsion containing waste waters are still being carried on.

The choice of the method for emulsive waste water treatment should be made in accordance with the local conditions of the enterprise. Here the ratio between emulsive effluent and the total effluent of the enterprise should be taken into consideration as well as the properties of the emulsions discharged and also the presence of free industrial areas. The final scheme of treatment should be confirmed by a technical-economic calculation.

ADVANCED WASTEWATER TREATMENT FOR AN ORGANIC CHEMICALS MANUFACTURING COMPLEX

by

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ABSTRACT

The Bound Brook plant of the American Cyanamid Company manufactures dyes, chemical intermediates, organic pigments, plastic additives, pharmaceuticals, fine chemicals, agricultural chemicals, elastomers and rubber chemicals. The plant's extremely complex wastewater stream now receives primary and secondary treatment. Because of State and Federal regulation and because of the effluent's impact on the receiving water, American Cyanamid is designing an advanced wastewater treatment system consisting of trimedia filtration and carbon adsorption to further treat the Bound Brook plant effluent. Alternative treatment processes were considered in paper studies and in laboratory bench scale studies and were rejected. Both filtration and carbon adsorption processes were tested in pilot studies, and selected versions of both processes are being further evaluated in on-going prototype demonstrations. The full scale system is currently under design, and the system will be fully operational in December 1977.

ACKNOWLEDGMENTS

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FIGURES

Figure No.	
1	Flow Diagram – Primary and Secondary Treatment Facilities
2	TOC Isotherm Plot
3	Flow Diagram – 5-In Diameter GAC Pilot Plant
4	TOC Breakthrough Curve
5	Flow Diagram – 30-In Diameter Pilot Column
6	TOC Removal – 30-In Diameter Column
7	Headloss Profile Without Coagulant Aid
8	Headloss Profile With Coagulant Aid
9	Cluster Filter Configuration
10	Flow Diagram – AWT Facilities

TABLES

Table No.	
1	Influent Wastewater Characteristics
2	Typical Removal Efficiencies in Biological Treatment System
3	5–In Diameter GAC Pilot Plant – Dissolved Solids Data
4	5–In Diameter GAC Pilot Plant – Ammonia and Organic Nitrogen Data
5	Powdered Activated Carbon Pilot Studies I – Performance Summary
6	Powdered Activated Carbon Pilot Studies II – Performance Summary
7	Summary of Pilot Filter Media

The Bound Brook, New Jersey plant of American Cyanamid Company employs 2,200 persons and produces over 1,000 different products including dyes, chemical intermediates, organic pigments, plastic additives, pharmaceuticals, fine chemicals, agricultural chemicals, elastomers and rubber chemicals. The multiple waste discharges from the production operations are combined with cooling water, sanitary sewage and storm water runoff from the plant area to form a single effluent stream that is processed in an existing waste treatment facility. Typical ranges of biochemical oxygen demand (BOD), chemical oxygen demand (COD), color and total organic carbon (TOC) in the raw waste stream are shown in Table 1.

TABLE 1
Influent Wastewater Characteristics

Parameter	Concentration Range
BOD	270–400 mg/l
COD	1,000–1,400 mg/l
TOC	260–350 mg/l
Color	400–600 CDAPHA units

Wastewater treatment has been a major part of the Bound Brook operation for over 30 years. As wastewater technology has progressed with time, the Bound Brook Plant has made significant improvements to its wastewater treatment facilities. Figure 1 shows a flow diagram of the existing facilities. In the late 1930's, a primary treatment plant was installed at a cost of $500,000. This plant included a 19 million gallon (7.2 x 10^4 cu m) equalization basin, a lime neutralization facility with a capacity to neutralize an equivalent of 30 tons (27.2 metric tons) of sulfuric acid a day, and a 60 million gallon (2.3 x 10^5 cu m) primary settling lagoon.

Beginning in 1949, extensive laboratory and pilot plant studies were initiated to procure desing data for the construction of an activated sludge treatment plant. This facility was built in 1957 at a cost of $4,500,000 and placed into operation in 1958. The secondary waste treatment facilities consist of six aeration basins, each having a capacity of 3-1/3 million gallons (1.3 x 10^4 cu m), six secondary clarifiers, and a chlorine contact chamber. In addition to treating its industrial waste, the Bound Brook plant provides secondary treatment for up to 5 mgd (1.9 x 10^4 cu m/day) a day of primary treated waste from a regional municipal wastewater treatment authority serving the region surrounding the Bound Brook plant. Our contract with the Authority will expire in 1977, and their wastewaters will not be included in our advanced wastewater treatment system.

Our present waste treatment facilities provide better than a 90% reduction in the BOD loading and approximately a 65% reduction in TOC and COD. The color bodies present in our raw wastes are resistant to biodegradation and as a result, little color is removed through our existing facilities. Table 2 summarizes the BOD, COD and TOC removals obtained in our treatment facilities.

FIGURE 1

WASTE TREATMENT PLANT FLOW DIAGRAM
AMERICAN CYANAMID COMPANY
BOUND BROOK, NEW JERSEY

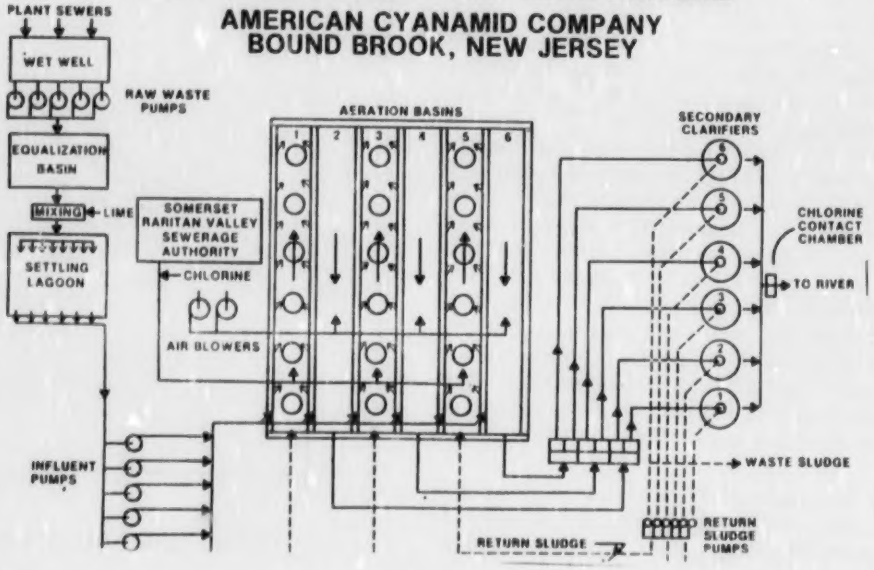


TABLE 2

Typical Removal Efficiencies in Biological Treatment System

Parameter	% Removal
BOD	90–95
COD	55–70
TOC	60–70

Unfortunately, many of the organic compounds present in our raw wastewater are resistant to biodegradation, and significant quantities of nonbiodegradable organics are present in our secondary effluent. In 1971 it became evident that additional treatment would be required, particularly for color, odor, toxicity and suspended solids.

For an understanding of the problem one must consider the relationship between the Bound Brook plant discharge and the flow in the receiving stream, the Raritan River. The Raritan River has an average flow of approximately 1 billion gallons per day (3.8 x 10^6 cu m/day) at the location of the Bound Brook discharge. Seasonal variations, however, can be significant. Minimum low flow is maintained at 90 million gallons per day (3.4 x 10^5 cu m/day) by release of water form an upstream reservoir. Under these low flow conditions which occur sporadically throughout the year, the Bound Brook plant effluent makes up approximately 25% of the river flow.

Two alternatives were considered for upgrading the Bound Brook plant effluent. They were: 1) heavier emphasis on at-source treatment or control in the manufacturing areas and, 2) additional end-of-pipe treatment (advanced wastewater treatment) to supplement biological treatment. Consideration was given to a study program to isolate and treat concentrated waste streams containing refractory organics within the manufacturing area. However, manpower requirements and costs for individual waste treatment facilities scattered throughout the plant would have been excessive. The constantly changing product mix, and the possibility of process upsets and spills during transportation of raw materials from building to building, contributed to the doubt that this effort would be worthwhile. It would have been extremely difficult to predict the effects of removing components from the main waste stream, particularly what new toxicants might be created by the admixture of waste streams that in themselves are nontoxic. As a result, it was decided to proceed with further investigation of advanced wastewater treatment techniques.

Preliminary literature reviews and bench scale studies were conducted to evaluate activated carbon adsorption, high lime treatment and ozonation. High lime treatment produced no significant reductions in either color or organic matter. Ozone requirements to reduce the color and refractory levels to those achievable with activated carbon were impractical. Capital and operating cost for an ozonation plant were well beyond that for an activated carbon treatment facility. However, carbon isotherms conducted during the preliminary development work indicated that carbon would substantially reduce color, foam and refractory organics.

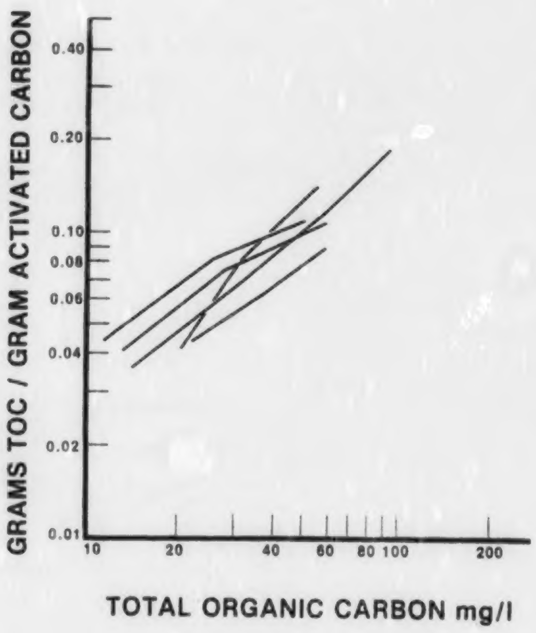
Since our preliminary isotherms were conducted in 1971, we have run approximately 100 additional isotherms on samples of our final effluent. Figure 2 shows the extreme variation in adsorption capacity of virgin carbon that is experienced with our particular wastewater.

Both granular and powdered activated carbons were investigated in pilot plant studies to evaluate the feasibility of their use of improving the Bound Brook effluent. Granular activated carbon (GAC) adsorption studies were conducted in pilot units consisting of four 6 ft x 5 in inside diameter (1.8 m x 12.7 cm) columns mounted on steel frames and piped with 1/2 in (1.3 cm) polyethylene tubing. The use of polyethylene tubing

FIGURE 2

TOTAL ORGANIC CARBON

ISOTHERMS



provided the flexibility for connecting the columns for either parallel or series operation as a particular test required. Figure 3 is a flow diagram of our GAC pilot system which was used for most of these studies. A side stream of clarified effluent taken from one of our existing clarifiers was pumped to a temporary storage drum and thence to the pilot columns. One set of columns was piped for parallel operation and packed with filtration media to prefilter the effluent for test Runs 2, 3 and 4. The second set of columns was packed with granular carbon and piped for either series or parallel operation depending on the test program. The adsorption data obtained from these studies were used to develop the process design for our full scale granular activated carbon facilities. During each of the runs, samples of effluent to the pilot plant system and effluent from each column were analyzed daily for TOC, COD, color and suspended solids.

Runs 1 and 2 were conducted for the purpose of obtaining breakthrough data for TOC, COD and color. For these runs, the 5-in (12.7 cm) diameter pilot plant was operated in a downflow packed bed mode with the four adsorption columns piped in series. For Run 1, the adsorption columns were fed unfiltered clarified effluent and were operated at a hydraulic loading rate of 1.9 gpm/sq ft (77.3 1/min/sq m). For Run 2, the influent was prefiltered through a mixed media of coal, sand and garnet before being fed to the adsorption columns. The flow rate for Run 2 was 3.4 gpm/sq ft (138 1/min/sq m). Figure 4 shows the breakthrough curve for TOC developed for Run 2.

In addition to the routine TOC, COD, color and suspended solids analyses, special samples from Run 1 were analyzed for dissolved solids, ammonia and organic nitrogen. Based on 20 analyses performed throughout Run 1, the average reduction in total dissolved solids through the adsorption columns was only 3%. Ammonia and organic nitrogen analyses were performed during the first 16 days of operation. During this period there was no observed reduction in the ammonia nitrogen concentration, however, there was an observed 85% reduction in the organic nitrogen concentration. Tables 3 and 4 summarize the dissolved solids, ammonia and organic nitrogen data collected through Run 1.

Exhausted carbon from Runs 1 and 2 was sent to an outside laboratory for regeneration studies and reused in succeeding runs. Run 3 was conducted to obtain adsorption data using a downflow moving bed system with regenerated carbon. The feed for this run was prefiltered. In the run, all four columns were initially charged with approximately 4 ft (1.2 m) of virgin activated carbon. As the carbon in the lead column became exhaused, the column was removed from service, repacked with regenerated carbon from Run 1 plus a 5% virgin makeup and placed back on stream at the end of the four column series.

5" DIAMETER GRANULAR ACTIVATED CARBON PILOT PLANT

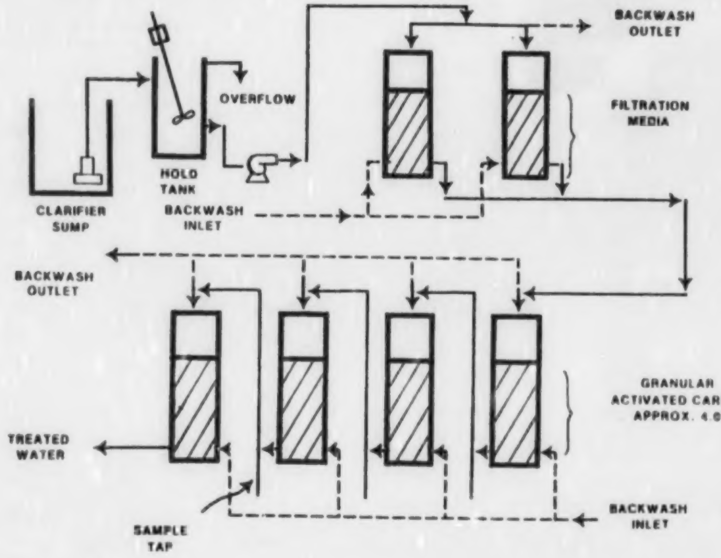
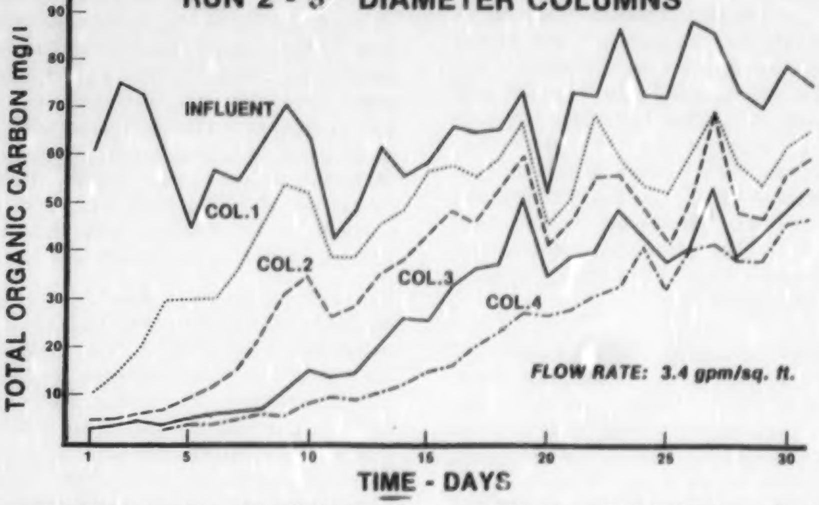


FIGURE 4

BREAKTHROUGH CURVE for TOTAL ORGANIC CARBON
RUN 2 - 5" DIAMETER COLUMNS



As part of our regeneration program, the efficiency of the regenerated carbon compared to virgin carbon was evaluated in order to establish design parameters for a full scale regeneration facility. Based on the information available in the literature at the time, we expected adsorption activity losses in the range of 10-15% based on one regeneration cycle. Comparisons of the once regenerated carbon with virgin carbon using the adsorption isotherms, indicated that activity losses in the range of 30-50% were being experienced. As a result, our pilot plant program was extended in order to conduct

TABLE 3
5-In Diameter GAC Pilot Plant –
Dissolved Solids Data

Cumulative Flow	Influent Concentration mg/l	Effluent Concentration mg/l
248	3,002	2,843
5,638	2,268	2,176
11,115	2,689	2,578
11,886	2,913	3,802
13,050	2,511	2,427
13,807	2,777	2,668
14,374	1,942	1,863
14,764	2,236	2,210
15,567	2,059	2,019
16,007	2,068	2,017
18,233	2,467	2,394
21,237	2,380	2,268
22,765	2,529	2,524
23,594	2,752	2,718
24,344	2,238	2,172
25,459	2,361	2,341
25,852	1,870	1,876
26,616	2,449	2,413
27,780	2,595	2,470
28,160	2,335	2,300
Average Concentration	2,422 mg/l	2,354 mg/l

Average Reduction = 3%

TABLE 4

5-In Diameter GAC Pilot Plant –
Ammonia and Organic Nitrogen Data

	Ammonia Nitrogen Concentration		Organic Nitrogen Concentration	
Cumulative Flow Gal	Influent mg/l	Effluent mg/l	Influent mg/l	Effluent mg/l
641	34	33	14	3
1,421	34	33	18	3
1,829	27	27	10	1
2,209	28	28	9	1
2,589	34	33	11	1
2,976	41	39	10	3
3,353	45	42	12	2
4,107	42	40	13	3
4,487	58	54	13	2
4,861	58	56	13	1
5,251	49	49	9	1
5,638	45	44	15	1
6,038	46	43	17	6
Average	41 mg/l	40 mg/l	13 mg/l	2 mg/l

additional column studies during which different carbons and regeneration conditions were evaluated for adsorption capacity through multiple regenerations. For these tests, the pilot columns were piped in parallel so that each column was fed the same wastewater. In each of the four exhaustion runs one column was used as a control and was packed with virgin carbon; a second column contained carbon that had been acid washed prior to regeneration using 1.5% hydrochloric acid solution; a third column contained regenerated carbon from the previous run without pretreatment; and the fourth column contained a competitive carbon which was being used for comparative purposes. Based on a comparison of adsorption capacities for total organic carbon after three cycles of regeneration, a carbon was found that could be regenerated to approximately 75-80% of its virgin adsorption capacity while keeping its physical losses to within 7%.

The use of powdered activated carbon to upgrade the Bound Brook plant effluent was also evaluated during two separate pilot plant studies. Both studies employed a process in which the controlled addition of powdered activated carbon (PAC) to aeration chambers in activated sludge units was evaluated. The studies were conducted using the Bound Brook primary treated effluent as feed to the activated sludge systems.

A preliminary PAC study was conducted during the first quarter of 1973. For this study the beneficial effects of adding low dosages of powdered activated carbon to our activated sludge system were investigated on a pilot scale. At the time of this evaluation, there were no proven techniques to separate exhausted powdered activated carbon from the biological sludge to regenerate it for reuse. The investigation, therefore, was based on the addition of powdered activated carbon on a throw-away basis. For this study two 115-gallon (0.44 cu m) capacity activated sludge systems were established. Both units were operated to simulate the existing activated sludge plant without the addition of the primary treated waste from the Somerset-Raritan Valley Sewage Authority.

The pilot plants were operated as plug flow units with a 20-hour detention time, a 30% return sludge ratio and a mixed liquor suspended solids concentration ranging from 3,500-5,500 mg/1. Following the initial start-up, the units were allowed to run for 22 days to reach steady state conditions and a stable BOD removal efficiency.

Four separate dosage levels; 42 mg/1, 84 mg/1, 126 mg/1 and 168 mg/1; of powdered activated carbon were evaluated in the pilot units. The second unit was operated as a control throughout the study. Table 5 summarizes the results of this 3-month study. In general, there were no significant reductions in the TOC or COD levels in the effluent of the powdered activated carbon system even at dosage rates of 168 mg of powdered carbon per liter of influent waste. The most significant improvement was in the color removal at the 168 mg/1 dosage level. The color removal efficiency was increased to 33% compared to a 7% level for the control unit. The residual color, however, averaged 331 CDAPHA units and was still readily noticeable. It was obvious from this preliminary investigation that much greater carbon dosage rates would be necessary in order to produce a powdered activated carbon system effluent that would be comparable to that achieved with granular activated carbon.

The second PAC process investigation was initiated in January 1974. At that time, powdered activated carbon had been successfully regenerated using a modified transport reactor. As a result of this work, the addition

TABLE 5
Powdered Activated Carbon Pilot Studies I – Performance Summary

Activated Sludge Unit	BOD Influent mg/1	BOD Effluent mg/1	BOD Removal %	TOC Influent mg/1	TOC Effluent mg/1	TOC Removal %	COLOR Influent CDAPHA	COLOR Effluent CDAPHA	COLOR Removal %
Control	263	19	93	205	77	62	414	430	(4)
PAC 42 mg/1		25	90		77	62		399	4
Control	350	12	97	280	73	74	452	398	12
PAC 84 mg/1		20	94		84	70		332	27
Control	333	24	93	254	81	68	417	450	(8)
PAC 126mg/1		13	96		73	71		341	18
Control	312	9	97	263	70	73	491	459	7
PAC 168 mg/1		9	97		60	77		331	33

PAC = Powdered Activated Carbon

of powdered activated carbon to the existing activated sludge plant at dosage rates in excess of 200 mg/l became attractive. The purpose of this second study was to determine the powdered activated carbon dosage requirements necessary to produce an effluent of similar quality to that obtained with granular activated carbon.

This study was conducted using four completely mixed biounits. Each unit consisted of a 6.3-liter aeration chamber and a 4-liter gravity clarifier section. Return sludge was drawn automatically from the clarifier bottoms into the aeration chambers. One biounit was set up as a control, and the other three were run at various powdered activated carbon feed concentrations. All four units were operated with an average detention time of 14 hours and a sludge age ranging from 10-14 days.

Powdered activated carbon feed rates ranging from 340 to 990 mg/l of carbon were investigated. Table 6 summarizes the results of this study. It was concluded that the powdered activated carbon process would require exorbitant carbon dosages in order to produce a final effluent with low color and TOC. It was further concluded that these dosage requirements were neither economical nor practical.

Data generated in the 5-in (12.7 cm) diameter column studies and the PAC studies were ultimately used to evaluate 17 possible alternative processes for upgrading the Bound Brook system. These processes included granular systems, powdered activated carbon systems and combined powdered/granular activated carbon systems. The most attractive process from a technical standpoint and a capital and operating cost was the upflow, expanded, pulse-bed design.

To further test this design a larger granular activated carbon prototype was installed in 1974. Figure 5 shows the flow diagram of the 30-in (76.2 cm) diameter pilot system. The carbon column is 30-in (76.2 cm) in diameter x 35 ft (10.7 m) on the straight side with a 60° cone bottom and is constructed of fiber glass. Filtered wastewater is pumped into the bottom of the column through five 1-in (2.5 cm) diameter nozzles located in the cone section. The feedwater passes up through the bed at a hydraulic flow rate of 8 gpm/sq ft (326 l/min/sq m). Each day a pulse of exhausted carbon ranging from 2.5 to 5%, depending on the organic loading, is removed from the bottom of the column, while an equivalent amount of fresh carbon is added to the top of the bed.

Currently, the column is only being pulsed at a 2.5% rate. The bed depth of the column is maintained at approximately 30 ft (9.2 m), thereby providing a detention time of approximately 30 minutes. Presently, the column is being pulsed using virgin carbon; however, by the end of the year, we will begin using regenerated carbon for pulsing. Our test program is designed to run through five complete cycles of regeneration with the carbon now being exhausted. Our purpose is to further optimize the regeneration conditions for our spent carbon and to better define the adsorption capacity of the carbon after several regenerations.

Exhausted carbon from this column is being regenerated in a 3-ft (0.92 m) diameter x 6-hearth multiple hearth pilot furnace. Figure 6 shows recent influent and effluent TOC concentrations to the column based on a 2.5% pulse. The TOC removal through the column for this period averaged 68%.

Initially it was planned to operate the advanced wastewater treatment system without filtration of the wastewater, and it was believed that the upflow expanded bed could accommodate the range of suspended solids loading anticipated from the secondary treatment system. However, two factors caused us to include a filtration system in our design: 1) stringent limitations placed by the EPA on our effluent suspended solids and 2) poor operating experience in our prototype carbon studies caused in part by high suspended solids levels in the secondary effluent.

The EPA imposed a suspended solid limitation of our wastewater discharge of 1,950 pounds per day (885

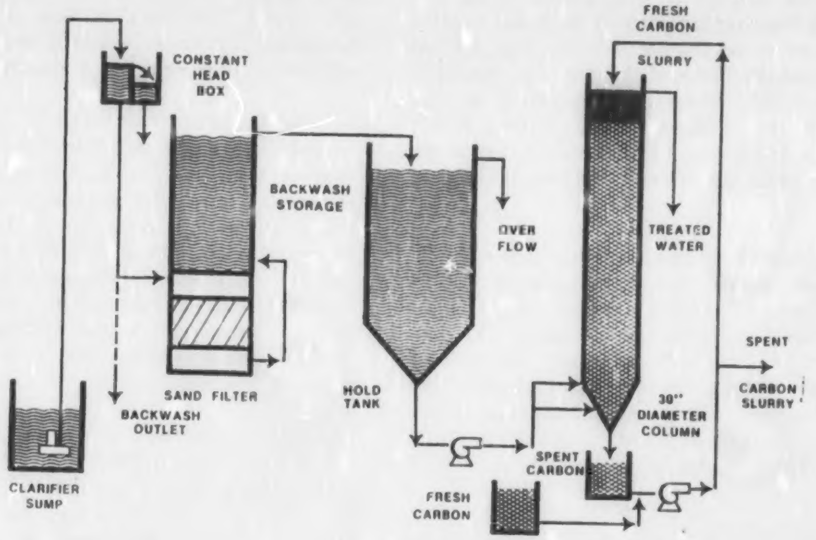
TABLE 6

Powdered Activated Carbon Pilot Studies II – Performance Summary

	BOD			TOC			COLOR		
Activated Sludge Unit	Influent mg/l	Effluent mg/l	Removal %	Influent mg/l	Effluent mg/l	Removal %	Influent CDAPHA	Effluent CDAPHA	Removal %
Control	366	21	94	261	114	54	502	515	(3)
PAC 340 mg/l		32	91		97	63		150	70
PAC 580 mg/l		28	92		76	71		94	81
Control	396	10	97	267	101	62	435	465	(7)
PAC 790 mg/l		8	98		34	87		73	83
PAC 990 mg/l		7	98		33	88		67	85

FIGURE 5

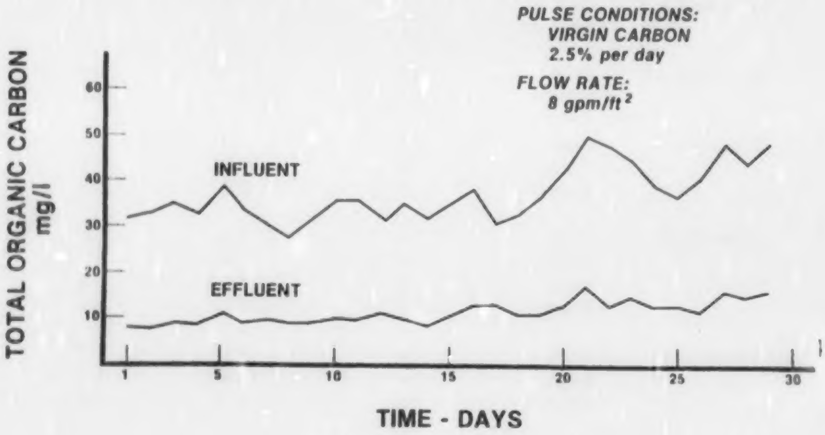
30" DIAMETER GAC PILOT PLANT SYSTEM


FRESH
CARBON
SLURRY
CONSTANT
HEAD
BOX
BACKWASH
STORAGE
OVER
FLOW
TREATED
WATER
SPENT
CARBON
SLURRY
SAND FILTER
BACKWASH
OUTLET
HOLD
TANK
30"
DIAMETER
COLUMN
SPENT
CARBON
CLARIFIER
SUMP
FRESH
CARBON

kg/day) daily average and 3,440 pounds per day (1,560 kg/day) daily maximum, which equates to 12 mg/1 daily average and 21 mg/1 daily maximum at a design flow of 20 mgd (7.6 x 10^4 cu m/day). Even with greatly improved control of the solids concentration in our aeration basins, we anticipate an average concentration of approximately 30 mg/1 suspended solids in the secondary effluent. Therefore, it was necessary to include filtration of effluent in our design.

The second factor was not anticipated and manifested itself only after the carbon prototype had been in operation for 5 days. Without warning, 13 ft (4.0 m) of the 28 ft (8.5 m) of carbon in the column was carried

TOTAL ORGANIC CARBON REMOVAL
30" DIAMETER PILOT CARBON COLUMN



out of the column by the effluent flow. This phenomenon occurred two more times during the initial runs without effluent filtration. It was postulated that solids accumulation in the lower portions of the carbon bed and the possible buildup of gas bubbles in the bed contributed to these carbon carry-overs. It was decided that the expense of wastewater filtration was justified because large carbon losses of the type just described would be intolerable in the full scale system. Therefore, independent of the regulatory considerations, it was decided to include a wastewater filtration system in our design and to place the system ahead of the carbon columns.

To determine the type of filtration system that will yield the best results at the least cost, three small pilot columns, an upflow prototype column and a larger prototype downflow column were utilized. The pilot columns were used primarily to select the type of filter media for use in a downflow configuration. The prototype filters were used to decide between an upflow and downflow configuration and to determine design parameters, utilizing the media type selected in the pilot columns.

The pilot columns were leased from a filter media supplier and consisted of 4-1/2 in (11.4 cm) diameter clear plastic columns with connections for operation in a downflow configuration and for backwashing with water. Three types of dual media and three types of trimedia were tested. The dual media consisted of a base layer of sand and a top layer of coal. The trimedia consisted of a bottom layer of garnet, a middle layer of sand, and a top layer of coal. Table 7 shows the grain size ranges of the sand and coal in the three types of dual media and the grain size ranges of the garnet, sand and coal in the three types of trimedia.

It was determined that trimedia Type C yielded the highest removal of suspended solids within an acceptable range of head loss. Not that this filtration media has a higher percentage of fine garnet than the other media tested, and closely resembles media typically used in water treatment. Examination of the suspended solids in the secondary effluent shows that the particles are smaller than those in a "typical" secondary effluent and that they lie within a very narrow range of particle sizes. This examination gives strength to the decision for small grain size filter media.

The upflow prototype unit consisted of a 16-in (40.6 cm) diameter column filled with 6 ft (1.8 m) of graded media ranging from coarse gravel to fine sand. Suspended solids removal efficiency, headloss buildup and breakthrough were determined both with and without coagulant aid. It was determined that the unit could be operated at rates up to 10 gpm/sq ft (407 l/min/sq m), but that breakthrough occurred without warning and

TABLE 7
Summary of Pilot Filter Media

Type	Component	Depth, In	Effective Size, mm	Uniformity Coefficient
Dual Media A	Coal	24	1.2	1.3
	Sand	10	0.5	1.3
Dual Media B	Coal	24	1.4	1.3
	Sand	10	0.5	1.3
Dual Media C	Coal	24	1.2-1.4	1.6
	Sand	12	0.6-0.7	1.7
Trimedia A	Coal	24	1.0	1.5
	Sand	9	0.45	1.5
	Garnet	3	0.2	1.5
Trimedia B	Coal	16	2.0	1.5
	Coal	8	1.0	1.5
	Sand	9	0.45	1.5
	Garnet	3	0.2	1.5
Trimedia C	Coal	16	1.0	1.5
	Sand	14	0.45	1.5
	Garnet	6	0.2	1.5

that the filter could not be backwashed sufficiently without expenditure of excessive amounts of energy and time. It was also determined that a gravity downflow configuration was more economical to install.

The large prototype downflow filter is 4 ft (1.2 m) in diameter and is 35 ft (10.7 m) high. The filter is provided with instrumentation to measure flow rate through the filter, headloss across the filter, differential pressure drop across 2-¾ in (7 cm) increments of bed depth and backwash flow rate.

Tests were run to determine optimal feed rate, suspended solids removal efficiency, headloss buildup, breakthrough and backwash water charactersitics. In addition, profiles of pressure drop through the bed were drawn to determine how much of the filter bed was being utilized and whether there was excessive headloss across the media interfaces. It was found that suspended solids removal efficiency varied from 64 to 84% at suspended solids feed concentrations varying from 16 to 37 mg/1. Headloss buildup was extremely slow with some filter runs exceeding 24 hours before the filter was backwashed. The filter was operated successfully at rates up to 8 gpm/sq ft (326 1/min/sq m). Figure 7 shows a typical headloss profile through the filter bed with no coagulant aid used. Note the peaks occurring at the media interface locations, indicating that substantial quantities of solids are being trapped at these interfaces. Figure 8 shows a typical headloss profile through the bed when a coagulant aid was used. Note that although solids removal efficiency remains high, the solids built up at the surface of the filter, and filter runs were drastically shortened.

It was decided from the results of the prototype studies that a downflow filter packed with trimedia would be used. Air backwash will be employed to ensure that the suspended solids trapped in the lower portions of the bed will be removed. The backwash cycle will be initiated by headloss buildup rather than solids breakthrough.

The results of all the paper studies, pilot tests and

FIGURE 7

HEADLOSS PROFILE WITHOUT COAGULANT AID

4' DIAMETER PILOT FILTER

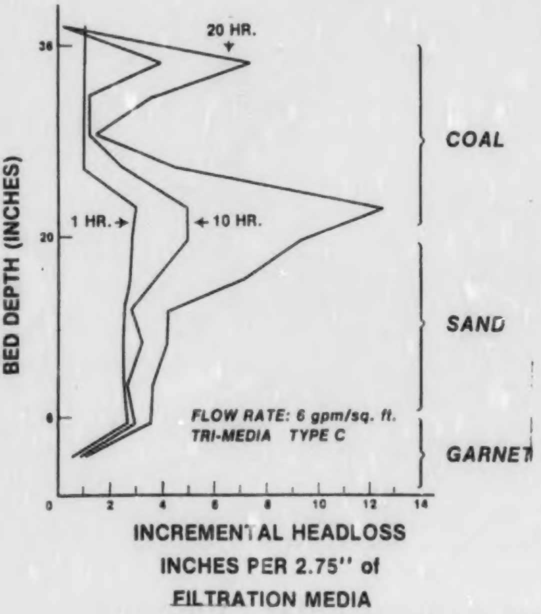
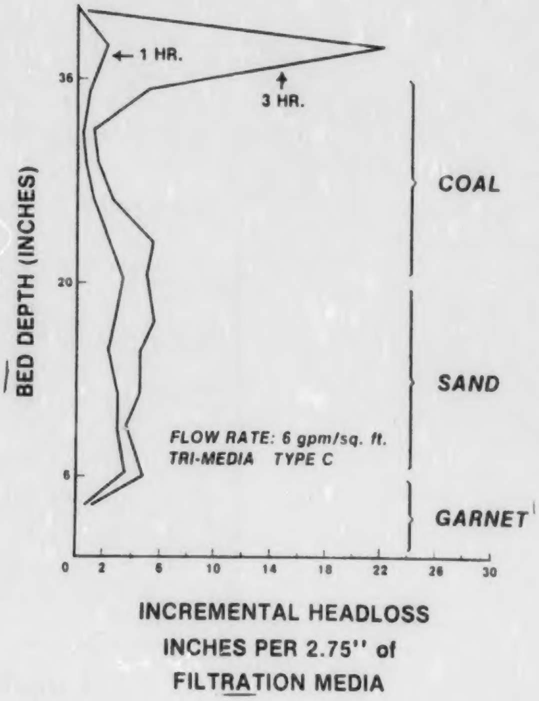


FIGURE 8

HEADLOSS PROFILE WITH COAGULANT AID

4' DIAMETER PILOT FILTER

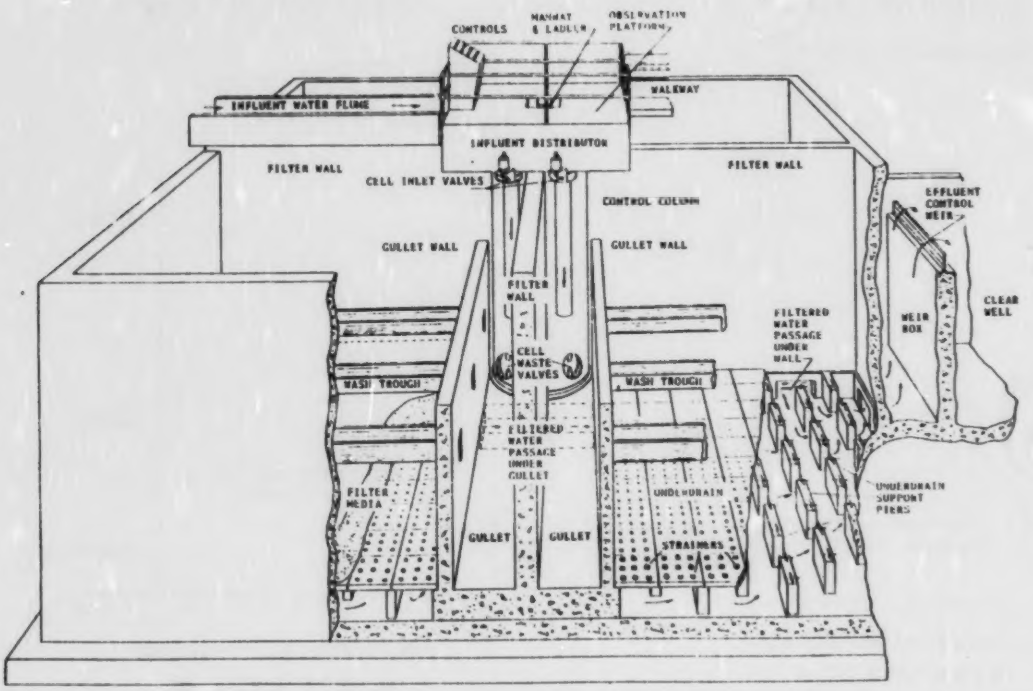


prototype studies were analyzed to determine design parameters for the full scale plant. The trimedia filters are designed for a hydraulic loading of 5 gpm/sq ft (204 1/min/sq m) with one filter cell out of service for backwashing. The backwash cycle will consist of drawing down of the liquid level in the cell being backwashed to within 6 in (15.2 cm) of the media surface, air scouring at a rate of 3-5 cfm/sq ft (0.9-1.5 cu m/min/sq m) for 5 minutes, air scouring at the same rate plus water backwashing at a rate of 3-5 gpm/sq ft (122-204 1/min/sq m) for 2-3 minutes, water backwashing alone at a rate of 15 gpm/sq ft (611 1/min/sq m) for up to 10 minutes, and gradually shutting off the backwash water over a period of 4 minutes in order to reclassify the filter media.

The physical configuration of the filters is shown in Figure 9, and is known as a cluster filter design. The actual filter will consist of two of these clusters with the flow split between them. Each cell of the cluster acts as an individual filter and can be isolated from the other seven cells. Each cell will be 22 x 23 ft (6.7 x 7.0 m), and will contain approximately 900 nozzles set at 9-in (22.9 cm) centers in a false bottom. Liquid flows into a splitter box located above the center column and divides evenly among the four cells in the cluster. Flow continues by gravity through the media and nozzles into a false bottom, then discharges into an effluent channel, and drops over a weir into a sump. When backwash is initiated by a high water level above the media, the water is drawn down through a siphon. Air is pumped into the false bottom, and is distributed evenly among the nozzles during the air scour. A water backwash is then initiated with water distributing evenly among the nozzles to complete the backwash cycle.

The carbon columns are designed for a hydraulic loading of 8 gpm/sq ft (326 1/mm/sq m) with 5% of the carbon bed volume being pulsed each day on the average. The physical configuration of the columns consists of ten 16-ft (4.9 m) diameter x 40-ft (12.2 m) straight side columns with 45° cone bottoms. The ten columns will be piped in parallel and will be charged with 30 ft (9.2 m) of carbon. Wastewater will be introduced to the bottom of each column through eight inlet ports projecting into the cone bottom. At the design hydraulic loading of 8 gpm/sq ft (326 1/min/sq m), a linear velocity of approximately 1 ft/min (0.31 m/min) will be

DOWNFLOW CLUSTER FILTER


CONTROLS
MANWAY & LADDER
OBSERVATION PLATFORM
WALKWAY
INFLUENT WATER FLUME
INFLUENT DISTRIBUTOR
FILTER WALL
CELL INLET VALVES
FILTER WALL
CONTROL COLUMN
EFFLUENT CONTROL WEIR
GULLET WALL
GULLET WALL
FILTER WALL
CLEAR WELL
WEIR BOX
FILTERED WATER PASSAGE UNDER WALL
CELL WASTE VALVES
WASH TROUGH
WASH TROUGH
FILTERED WATER PASSAGE UNDER GULLET
UNDERDRAIN SUPPORT PIERS
FILTER MEDIA
UNDERDRAIN
GULLET
GULLET
STRAINERS

Courtesy of General Filter Company

experienced, and a contact time of 30 minutes will result. The carbon bed is not restrained vertically, and operates as an upflow expanded bed. A unique feature of this design is that spent carbon can be removed simultaneously with the addition of fresh carbon without altering the flow rate through the column. The pulse design allows operation of the columns in a manner that approximates countercurrent movement of the wastewater and carbon, thereby providing efficient utilization of the carbon.

Figure 10 shows the general arrangement of the components of the advanced wastewater treatment system, including the carbon transport system and carbon regeneration system. A spent pulse of carbon will be transferred as a slurry to a spent carbon storage tank and then to a dewatering screw. The dewatering screw will permit the carbon to drain to approximately 50% moisture before it is fed into the 26-ft (7.9 m) diameter multiple hearth furnace for regeneration. The spent carbon will be regenerated thermally in a closely controlled atmosphere and temperature profile with a maximum temperature of approximately 1,750°F (954°C). Steam will be injected into the furnace to enhance the reactivation step. Following regeneration, the carbon will be water quenched to reduce the temperature to below 100°F (38°C). From the quench tank, the carbon will be transferred to the regenerated carbon storage tank for reuse in the system.

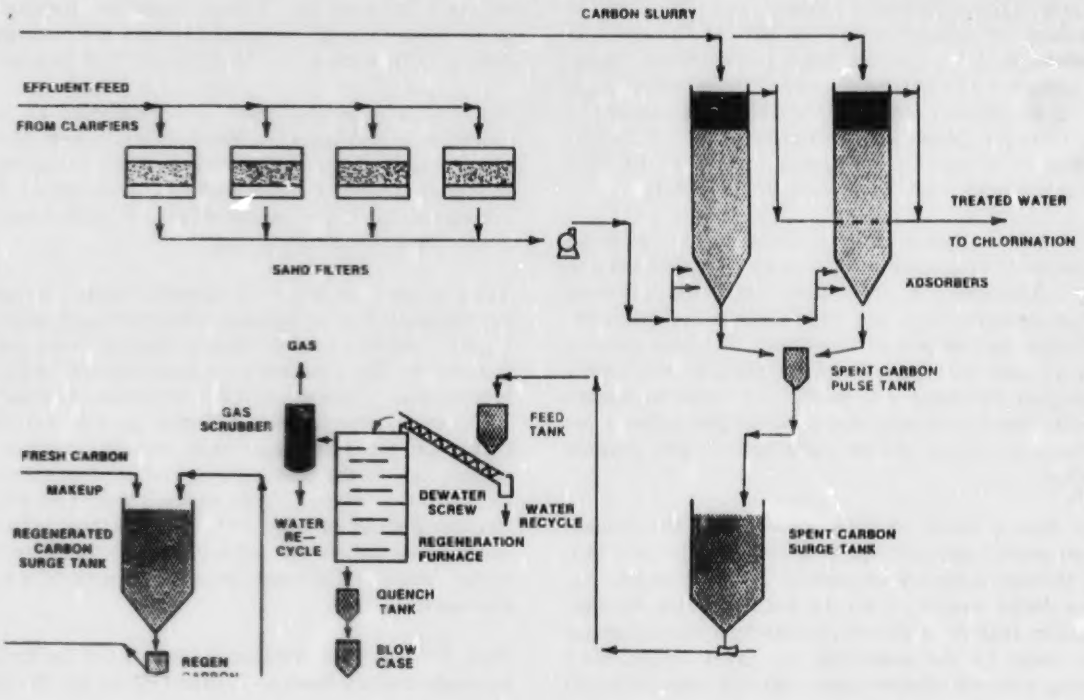
Under average loading conditions, approximately 100,000 pounds (45,400 kg) of carbon per day will be regenerated. Carbon attrition losses are estimated to be 7% per cycle, so that an estimated 7,000 pounds (3,180 kg) of virgin carbon will have to be added daily to maintain the carbon inventory. The total carbon inventory in the system will be 2.5 million pounds (1.14 x 10^6 kg).

Construction of the advanced wastewater treatment facilities and a waste activated sludge disposal plant will begin in the first quarter 1976.

Mechanical completion is scheduled for June 1977 with standard operation in December 1977. The capital cost for these facilities is estimated to be $22.4 million and will bring the total capital investment for water pollution control for the Bound Brook plant to over $35 million. Operating cost for water pollution control facilities will exceed $8 million per year.

FIGURE 10

AWT


CARBON SLURRY
EFFLUENT FEED
FROM CLARIFIERS
SAND FILTERS
TREATED WATER
TO CHLORINATION
ADSORBERS
SPENT CARBON
PULSE TANK
GAS
GAS
SCRUBBER
FEED
TANK
FRESH CARBON
MAKEUP
DEWATER
SCREW
WATER
RECYCLE
WATER
RE-
CYCLE
REGENERATED
CARBON
SURGE TANK
REGENERATION
FURNACE
SPENT CARBON
SURGE TANK
QUENCH
TANK
BLOW
CASE
REGEN

Cost Benefits of Physical Chemical Treatment

by Frank P. Sebastian Senior Vice President
Envirotech Corporation

The Clean Water Act of 1972 established a national goal and a national policy for the United States. So far as industrial water pollution control is concerned, it established a timetable of 1977 for the best practicable control technology, and 1983 for the best available control technology.

In the municipal sector, the 1977 timetable is for secondary treatment, with water reclamation and reuse factors to be considered after June 30, 1974, and by 1983 the best practicable technology.

In summary, the Act calls for clean streams for swimming, recreation, and the safety of fish and wildlife, by 1985, with full consideration for reclamation and reuse possibilities for projects after mid-1974.

The technology exists today to more than meet all the municipal wastewater requirements. Accordingly, guidelines have been issued for most industrial effluent categories. Any list of examples of advanced waste treatment that might be utilized to bring the nation to the fruition of its water pollution control goals would include Tahoe, Colorado Springs and Windhoek as instances of existing plants, as well as Occoquan in Washington, D.C.; Garland, Texas, and numerous others, as examples of advanced treatment plants under design and construction in the U.S. Overall there are some 113 plants under design or construction utilizing various aspects of advanced waste treatment to meet the 1977 goals previously established under the 1972 Act.

Let's take a closeup look at Colorado Springs as an example of upgradability of present biological technology, flexibility for the future utilization of more advanced technology, and water reclamation and reuse. Colorado Springs was an overloaded 30-million gallon a day primary secondary treatment plant to which more biological treatment was added. The Colorado Springs facility has also incorporated a two-million gallon a day tertiary treatment system utilizing lime and granular carbon.

The lime is added to a Reactor-Clarifier, the effluent from which passes through a multi-media filter and then on through a battery of granular carbon columns. The lime sludge removed from the bottom of the Reactor-Clarifier tank is recalcined in a multiple hearth furnace for reuse. In the same way, the spent carbon, after having removed soluble organic material, trace pesticides and refractory organics from the effluent, is regenerated on site with losses as low as 3% and averaging only 5-7%.

The resulting product from the Colorado Springs Water Reclamation plant is a good indication of the potential payoff that can result from the nation's newly adopted water pollution goals. The reclaimed water was planned to be piped to an electric power station for use as cooling water makeup. The reclaimed water is valued at 26¢ to 28¢ per thousand gallons, or about 30% discount from the wholesale value of water in Colorado Springs of 38¢ per thousand gallons. This proposed selling price compares favorably with the wholesale cost of water in my own San Francisco Bay Area.

To give you some indication of the potential need for such water, I should like to draw on a 1968 survey of the Great Lakes Basin conducted by the U.S. Department of Commerce. The study assumed high achievement in water conservation by industry and found that water depletion in the Great Lakes Basin could become a serious constraint to industrial expansion. By the year 2000 the vast Great Lakes Basin, which of course includes metropolitan Chicago, could be evaporating more water through its industries than the metropolis now withdraws from Lake Michigan for all of its uses.

The Colorado Springs plant, the installation at Lake Tahoe, and the Windhoek, Namibia (South West Africa) plant, which produces tap water, are all examples of biological treatment plants that have been upgraded to produce an ultra-high quality effluent through means of a physical chemical tertiary stage.

There is another phase of advanced waste treatment development that is equipment-intensive and relies on physical chemical rather than biological processes of wastewater. These processes are frequently referred to as independent physical chemical treatment systems or IPCT; even through some biological growth inevitably occurs on the surfaces of such process materials as carbon. One of the basic independent physical chemical designs is that of the EPA as set forth in its Technology Transfer Bulletin of July 1971. This flowsheet, which is almost identical to the tertiary stage at Tahoe or the tertiary stage at Colorado Springs, is worthy of a brief explanation.

First, I direct your attention to the area of the middle rectangle marked Reactor-Clarifier (Figure A). The first step in the process is to separate the liquids and solids by the use of gravity and lime. This is done in a two-stage process involving sedimentation equipment such as a Reactor-Clarifier. The lime is mixed with raw influent, not secondary effluent, as it enters the Reactor-Clarifier. The lime facilitates the settling of the solid material and the clarification of the effluent. It also renders the phosphates insoluble which promotes settling. The carbon dioxide, shown entering this basin, is used to neutralize the water after it has been made highly alkaline through the addition of lime. The CO_2 source will be explained later. The output of this separation step consists of chemically clarified water, which is shown coming off to the top right; and the settled solids, that is, sludge and lime, which are shown coming down from the bottom of the basin. The lime that was used in the Reactor-Clarifier is reclaimed in a multiple hearth furnace reclamation process which produces the needed CO_2 as a product of the stack gas. Thus, the furnace stack gas, which approaches zero air pollution levels, provides the carbon dioxide, which is shown as it is bubbled back through the water to neutralize it, as mentioned earlier.

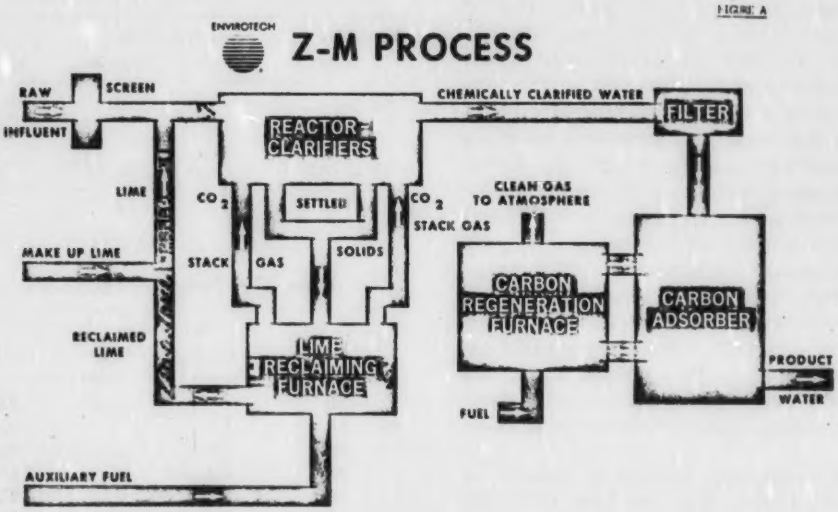
The principle product of the multiple hearth lime reclaiming furnace, which is called a Plural Purpose Furnace, and on which Envirotech has process patents, is the reclaimed lime, which combined with makeup lime, is recycled in the process. In this step the insoluble DDT, PCB, and indeed all the chlorinated hydrocarbons that settle out are decomposed and removed from the environment. Additionally, there is a certain amount of ash coming off the lime reclaiming furnace which will be discussed later.

Although a principal source of energy in the lime reclaiming furnace is the fuel value contained in the sludge solids removed from the wastewater, auxiliary fuel is required. The fuel traditionally burned has been natural gas. However, due to the developing natural gas shortage, an alternative fuel burning capacity will be needed. A Hydroburner has been developed for use in multiple hearth and Plural Purpose furnaces which is capable of burning #2, #4 and #6 oil fuels. The normal 4:1 turndown ratio, flame stability and system control have been achieved with this new burner. This innovation is expected to further enhance the practicability of recalcining lime while also reducing operating expenses.

The next step in the liquid stage is for the chemically clarified water to be piped to a multi-media filter, which functions to capture any suspended solids that remain after lime treatment and neutralization. This filtration prevents carryover onto the carbon column step which follows.

The carbon adsorption and regeneration phases come next. These processes are the same as the ones that have been used so successfully at the Lake Tahoe plant since 1965. These are the steps that remove the taste, odor, color, detergents, inorganics including the solvable problems of pesticides, chlorinated hydrocrabons, and trace organics from the wastewater. After the carbon polishing phase, the final product water is either chlorinated and put to use, or perhaps returned to the water course. The spent carbon, laden with the dissolved material it has adsorbed from the wastewater in the next to last stage of treatment, is regenerated on site in a multiple hearth furnace. During this regeneration process, the organic material is pyrolyzed or distilled off the carbon and is then totally oxidized before being scrubbed and exhausted so that the only highly cleansed air is released into

FIGURE A



the atmosphere. It is this regeneration step that the final trace amounts of pesticides, which were removed from the water, are decomposed and thus, eliminated from the environment.

PCBs, which are the most thermally resistant of these materials, are appearing in the natural environment in increasing quantities. According to the October 10, 1975 issue of Wall Street Journal, "Persistent PCBs loom as a worse menace than DDT." PCBs have recently proved more resistant to natural degradation than DDT. Many areas now have PCB accumulations exceeding those of DDT. Additionally, researchers have discovered that these substances are more toxic than previously thought. In fact, the maximum allowable PCB feed concentration of 5 ppm, as set by the Food and Drug Administration in 1973, is presently considered unsafe by many scientists. A number of animal studies substantiate the acute toxic effects of PCB. For instance, a study reported by the Wall Street Journal article previously mentioned found increased incidence of morbidity in primates fed PCB doses of only 2.5 ppm. PCBs have proliferated so widely that they are even being detected in artificial lakes having no link to either municipal or industrial effluents. Such a lake is ten-year old Lake Anne in Reston, Virginia, where fish samples were found having accumulated significant concentrations of PCBs (1). Samplings of trout and salmon from Lake Michigan have averaged 22.9 and 10.5 ppm of PCB, respectively. Fish samples from the waters of the Hudson, Ohio and Milwaukee rivers have also shown worrisome PCB levels.

However, the problems associated with PCBs can be reduced through sound technological practices. One of the best economical methods for disposing of PCBs is through the normal incineration procedure in multiple hearth furnaces. Tests show that 99.9% of PCBs are decomposed in the multiple hearth furnace at 1100°F using a 0.1 second exhaust gas detection time (2). Indeed, according to a United States Geological Service survey, there appears to be no other way of removing these highly persistent materials from the natural environment – except in a sewage treatment plant which has a furnace incorporated into its treatment process. One of the recently determined benefits of the total oxidation of sludge in the multiple hearth furnace is that 95% of the PCBs are destroyed in the normal operation temperature of the sludge furnace – which is only 700°F using a 0.1 second exhaust gas retention time. This lowered temperature represents a substantial fuel savings compared to alternate methods, while at no additional expense it destroys 95% of PCB pollutants and also complies with EPA recommended performance standards for furnaces burning sludges found to contain PCBs.

To illustrate how incinerators perform in terms of air pollution standards, I quote from the June 1975 EPA Technology Transfer publication (4), "Air Pollution Aspects of Sludge Incineration," which states:

> ". . . the newly promulgated Federal NSPS (New Source Performance Standards) are based on demonstrated performance of an operating facility, indicates that use of proper emission controls and proper operation of the incineration system will enable a facility to meet all existing particulate matter regulations."

In connection with a Livermore, California, treatment facility, the San Francisco Bay Area Air Pollution Control District, one of the most stringent air pollution control districts in this country, rules that multiple hearth incinerators are an insignificant source of air pollution (5).

The toxicity of metals has caused increasing concern over their discharge in recent years. In response to the dangers of toxic concentrations of metals entering potable water supplies, plus the risks from biomagnification, the EPA has promulgated standards for metals discharge (6, 7). IPCT processes like the EPA flowsheet mentioned and high lime-carbon processes have demonstrated the removal of substantial quantities of toxic and undesirable metals from wastewater. A study by Maruyama et al. (8) used various pilot plants to evaluate raw sewage metal removal efficiency using IPCT processes. A high and a low lime system were utilized. The high lime system used a lime concentration of 600 mg/l with a resultant pH of 11.5, while the low lime system used a lime concentration of 260 mg/l and 20 mg/l of ferric sulfate with a resultant sludge pH of 10. The results of this study are summarized in Tables I and II. The "new"

TABLE I

Removal of Metals by Low Lime System

Removal (%)	With New Carbon Column	With Old Carbon Column
80 – 85	As	As, Cr^{+6}
85 – 90	Zn	Zn, Cn
90 – 95	Mn	
95 – 100	Cr^{+3}, Pb, Ni, Cr^{+6}	Cr^{+3}, Pb, Ni

TABLE II

Removal of Metals by High Lime System

Removal (%)	With New Carbon Column	With Old Carbon Column
75 – 80		Zn
80 – 85	Ba	As
85 – 90	Zn As	Ba
90 – 95	Cu, Hg	Cu, Hg
95 – 100	Cr^{+3}, Pb, Ni Mn, Cd, Cr^{+6}	Cr^{+3}, Pb, Ni Mn Cd Cr^{+3}

carbon column was a virgin carbon column, while the "old" carbon column had been in operation about a year and was described as needing regeneration. Notice that although each process has different removal efficiencies for particular metals, the removal efficiencies are generally greater than 90% for both lime processes.

A physical chemical process that is, again, similar to the Tahoe tertiary phase is the high lime-carbon adsorption process, which has been demonstrated full scale at the South Tahoe Water Reclamation plant (9). Several full scale municipal plants that will use this process are now under construction. Although not ideally suited for waste streams, where suitable, there are numerous advantages of using independent physical chemical treatment processes over conventional biological treatment. An important advantage of this process, and indeed all lime carbon IPCT processes, is that they are not susceptible to toxic or shock loads as is the case with conventional biological treatment plants.

Another variation of the high-lime carbon adsorption process is being installed in California at the Central Contra Costa Water Reclamation Project plant. Scheduled for completion in early 1976, the 30 mgd plant, with an ultimate design capacity of 120 mgd, will incorporate both the lime addition to raw sewage and recalcination processes, but in a modified flowsheet. In this modified process, removal of both metals and organics occurs in the recalcining process. As I mentioned earlier, the principal product of the Plural Purpose Furnace is reclaimed lime, which comes from sludge heavily laden with organics, phosphorus, metallics and other toxic substances. To avoid the overloading on the solids processing, these substances are removed from the lime-containing sludge before the recalcination step. This separation and removal process prevents the solids processing facility from being overloaded by metals, organics and other inerts. Incidentally, pilot test results for the Central Contra Costa Sanitary District plant found that the removal of suspended solids and biological oxygen demand was 99%, while phosphorus and nitrogen removal efficiencies were 96% and 94%, respectively (10).

Ash, mentioned previously, which is a major product of both lime reclaiming and sludge incineration, is being used experimentally at both Lower Allen Township, Pennsylvania, and Japan for fertilizer. Ash could also be utilized for such purposes as building materials, and perhaps even to aid in the salting of winter roads. Table III contains some typical analyses of ash taken from a tertiary sewage treatment plant.

The unique cost saving benefit using independent physical chemical treatment for primary treatment in new plants seeking to achieve clean water goals, is in terms of making an equipment investment that can meet long term objectives of higher quality effluent. This savings can be demonstrated by looking at some cost comparisons.

Since the purpose of this discussion is to investigate the costs of traditional primary secondary and tertiary treatment, hereafter called "tertiary", to independent physical chemical treatment, IPCT, a hypothetical "average" wastewater was used. The plant influent parameters are presented in Table IV. It is recognized that such an average waste stream does not exist, except for comparative purposes. Costs were estimated using the economic criteria set forth in Table V, and were derived through the use of the Envirotech computer program (11). In no way are the costs considered precise or totally reflective of the actual expenses, but rather the level of accuracy has been designed for comparative analyses. The predicted experimental error for capital costs are ± 10%, while the operational costs are believed to vary ± 15%.

TABLE III

TYPICAL ANALYSIS OF ASH FROM TERTIARY QUALITY ADVANCED WASTE TREATMENT SYSTEM

	Percent of Total	
Content	*Sample 1* *Lake Tahoe* *11/19/69*	*Sample 2* *Lake Tahoe* *11/25/69*
Silica (SiO_2)	23.85	23.72
Alumina (Al_2O_3)	16.34	22.10
Iron oxide (Fe_2O_3)	3.44	2.65
Magnesium oxide (MgO)	2.12	2.17
Total calcium oxide (CaO)	29.76	24.47
Available (free) calcium oxide (CaO)	1.16	1.37
Sodium (Na)	0.73	0.35
Potassium (K)	0.14	0.11
Boron (B)	0.02	0.02
Phosphorus pentoxide (P_2O_5)	6.87	15.35
Sulfate ion (SO_4)	2.79	2.84

TABLE IV
Raw Stream Characteristics

BOD_5	250 mg/l
COD	450 mg/l
Flow	30 mgd
Suspended Solids	250 mg/l
Alkalinity and Hardness	250 mg/l as $CaCO_3$

TABLE V

Economic Criteria

Item	Basis	Rate
Labor	Amounts per unit from (1) 168 hr/wk, 52 wk/yr	$5/hr (3.8 rubles/hr)
Benefits		20% of labor
Fuel		$2.80/million Btu (w kopecks/ million kg meters)
Power		2¢/KWH (4.1 kopecks/ million kg/m)
Maintenance Labor	Amounts per unit from (1)	$5/hr (3.8 rubles/hr)
Supplies	Amounts per unit from (1)	
Solids Disposal Hauling		$10/ton (.8 kopecks/kg)
Amortization	25 years	7% interest
Lime, virgin		$40/ton (3.4 kopecks/kg)
Carbon, virgin		47¢/lb (78.7 kopecks/kg)
Carbon makeup		8%/cycle
Lime recalcination Rate		90%

For comparative purposes, the discussion to follow uses two biological flowsheets, primary-secondary and tertiary, and compares their costs to those of similar process levels using IPCT treatment flowsheets. The traditional primary-secondary treatment with phosphorus removal includes primary clarification followed by waste activated treatment, lime precipitation of phosphorus, and pH adjustment to 7 by two-stage recarbonation, collection, recalcination plus recycle of lime solids, heat treatment and the incineration of sewage sludge solids (see Figure B). The biological tertiary flowsheet with phosphorus removal includes all the steps of the primary-secondary flowsheet with the addition of filtration and carbon adsorption (regeneration and recycle of granular carbon) (see Figure C).

The IPCT-I flowsheet includes lime treatment followed by pH adjustment to 7 by two-stage recarbonation, filtration, single-stage carbon adsorption, carbon regeneration, lime recalcination with recycle, and filtration plus the incineration of sewage sludge solids (see Figure D). The upgraded IPCT-II flowsheet is the same as IPCT-I except for the inclusion of additional carbon columns. The design of the primary-secondary flowsheet was to accomplish an 80% BOD_5 removal, while the tertiary flowsheet would remove 95% BOD_5. Comparatively, the predicted performance of the IPCT-I flowsheet was for 80% BOD_5 removal, while a 95% BOD_5 removal was the estimated result assumed from the IPCT-II flowsheet – having the extra carbon columns.

Cost increases, in particular fuel, which have dramatically escalated since 1970, are responsible for increasing the relative costs of PCT more appreciably than those for biological treatment. However, IPCT, where applicable, still offers significant cost saving opportunities over biological treatment. The cost estimates which follow do not include the savings that would be realized from utilizing such cost reducing equipment as the previously mentioned hydroburner, which would lower costs on the energy intensive PCT process.

First, let's compare the cost of traditional secondary treatment with phosphate removal to the lime-carbon process which is, again, similar to the EPA process, both of which can be operated in a mode to yield a secondary quality effluent. Looking at capital costs, we see that the traditional secondary treatment with phosphate removal for the 30 million gallon per day plant costs $24.6 million, while the IPCT-I plant is slightly higher – at about $25.1 million.

The operations and maintenance cost (including 7% amortization for 25 years) is only slightly favored in biological treatment processes (having phosphate removal) which cost 49.1¢/1000 gallons. The price for operating and maintaining this IPCT-I process is 3.5¢ more, or 52.6¢/1000 gallons, only 7% more than the biological alternative. However, with long term clean water goals now defined, let's compare the investment cost of IPCT versus biological treatment.

FIGURE B

PRIMARY-SECONDARY TREATMENT WITH PHOSPHOROUS REMOVAL

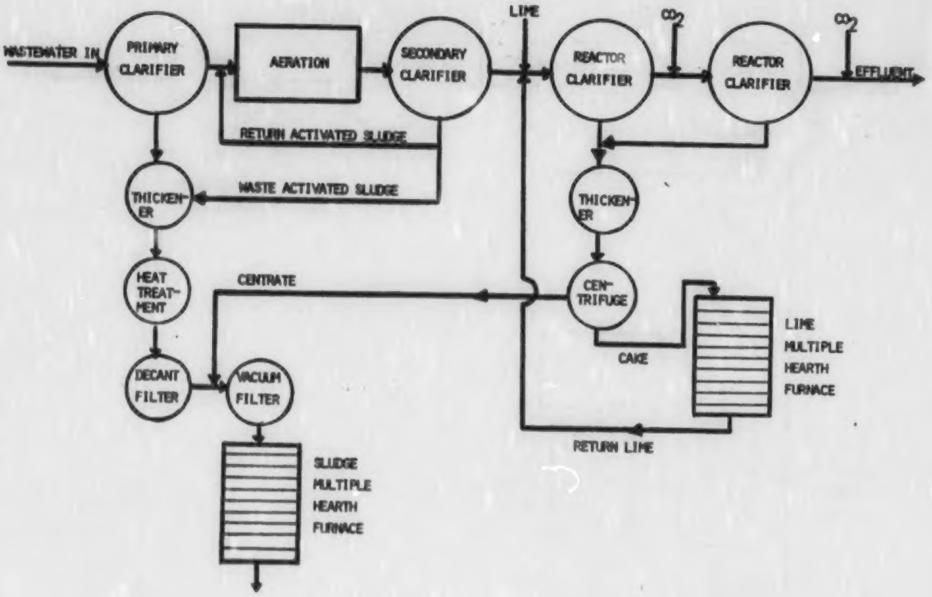

WASTEWATER IN
PRIMARY CLARIFIER
AERATION
SECONDARY CLARIFIER
LIME
REACTOR CLARIFIER
CO_2
REACTOR CLARIFIER
CO_2
EFFLUENT
RETURN ACTIVATED SLUDGE
WASTE ACTIVATED SLUDGE
THICKENER
HEAT TREATMENT
CENTRATE
DECANT FILTER
VACUUM FILTER
SLUDGE MULTIPLE HEARTH FURNACE
THICKENER
CENTRIFUGE
CAKE
LIME MULTIPLE HEARTH FURNACE
RETURN LIME

FIGURE C

PRIMARY-SECONDARY-TERTIARY TREATMENT PLANT

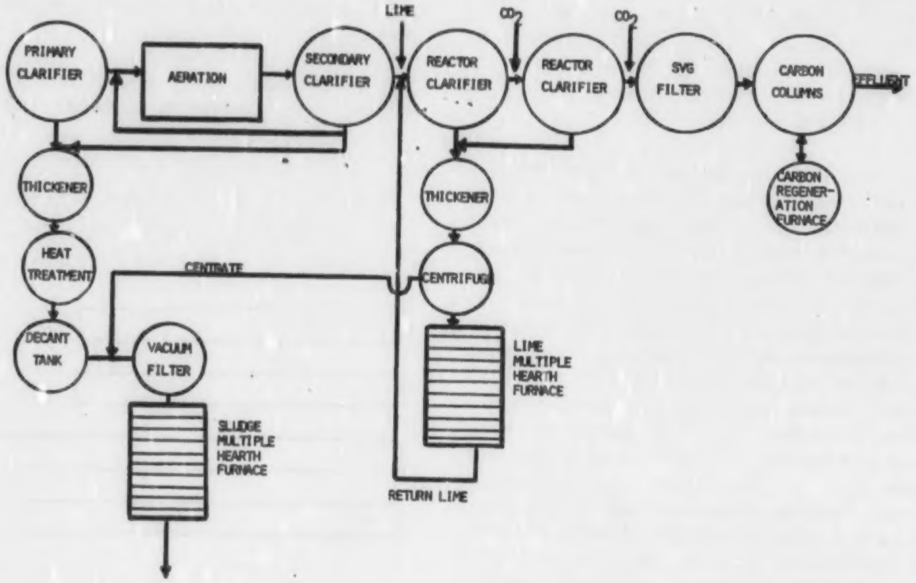
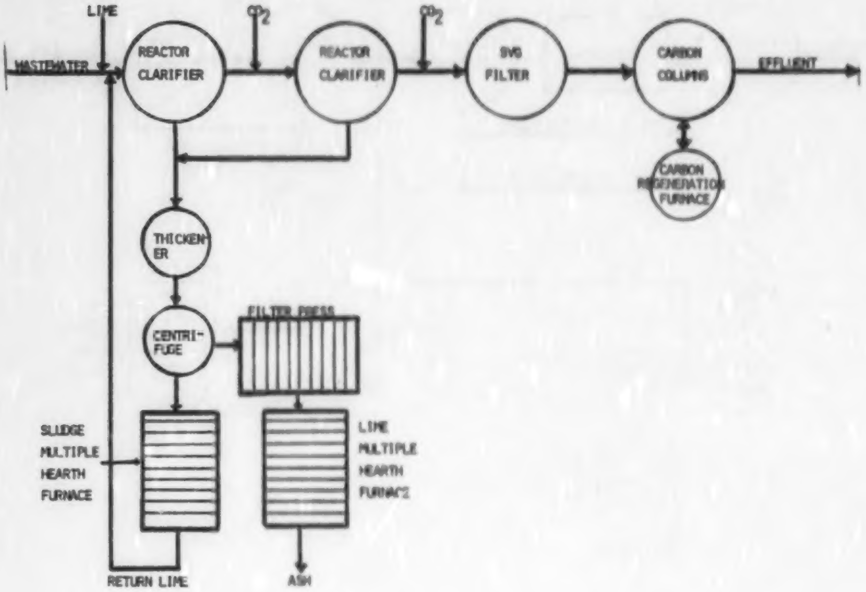

PRIMARY CLARIFIER
AERATION
SECONDARY CLARIFIER
LIME
REACTOR CLARIFIER
CO_2
REACTOR CLARIFIER
CO_2
SVG FILTER
CARBON COLUMNS
EFFLUENT
CARBON REGENERATION FURNACE
THICKENER
HEAT TREATMENT
CENTRATE
DECANT TANK
VACUUM FILTER
SLUDGE MULTIPLE HEARTH FURNACE
THICKENER
CENTRIFUGE
LIME MULTIPLE HEARTH FURNACE
RETURN LIME

FIGURE D

PHYSICAL CHEMICAL TREATMENT PLANT


LIME
WASTEWATER
REACTOR CLARIFIER
CO_2
REACTOR CLARIFIER
CO_2
SVG FILTER
CARBON COLUMNS
EFFLUENT
CARBON REGENERATION FURNACE
THICKENER
CENTRIFUGE
FILTER PRESS
SLUDGE MULTIPLE HEARTH FURNACE
LIME MULTIPLE HEARTH FURNACE
RETURN LIME
ASH

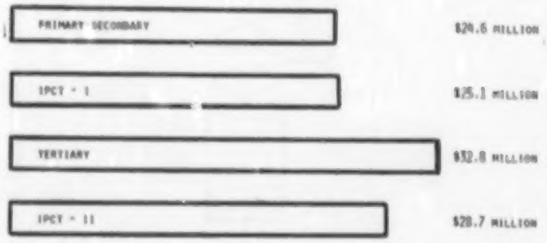
Two processes which have been shown to produce a "drinkable quality" water are traditional primary-secondary and tertiary treatment, and independent physical chemical treatment, IPCT-II (where applicable). The capital cost of the tertiary process is $32.8 million for a sample 30-million gpd plant, as compared to $28.7 million for the IPCT-II plant. The operating cost, including amortization, of the tertiary plant is 63.2¢/1000 gallons as compared to only 58.5¢/1000 gallons for the IPCT-II process.

Clearly, the benefit an independent physical chemical plant has over a conventional secondary plant is when the new standards take effect and require higher treatment levels, the required upgrading is more economical. The cost of adding equipment to a 30 mgd biological primary-secondary plant for upgrading to tertiary treatment quality are $8.2 million, while operating and maintenance expenses including amortization rise $1.5 million annually. Improving a 30 mgd IPCT facility from secondary to tertiary treatment costs only $3.6 million (2.7 million rubles) for equipment, while maintenance plus operations including amortization rises $0.6 million per year. The difference in construction costs between a biological primary-secondary plant and an IPCT-I plant is only $0.5 million, while the operating and total maintenance costs are larger by only $0.4 million annually. Considering that it takes $8.2 million to upgrade a biological plant to tertiary treatment, the $3.6 million needed for the similar upgrading of IPCT systems represents a sizable savings – $4.6 million. This large cost savings handsomely makes up for the small cost advantage that primary-secondary plants initially have over IPCT facilities. Figure E depicts this relationship.

Further illustrating the cost benefits of IPCT, is the $0.5 million yearly savings in operating and maintenance

FIGURE E

30 MGD WASTETREATMENT PLANT
CONSTRUCTION COSTS



costs encountered in IPCT-II facilities over biological plants having tertiary treatment (carbon columns) added. Water reclamation, which is now being seriously considered by more industries and communities in both the U.S. and Soviet Union, can be a cost effective procedure for IPCT plants. The California State Water Resources Control Board considers the cost of reclaimed water as reflective of collection and treatment expenses incurred through the secondary level of treatment. Since this is mandated into law, utilizing this concept yields reclaimed water at less than half the price from our sample IPCT-II plant (where the influent is applicable) compared to the same water from the tertiary flowsheet discussed. The cost for tertiary plant reclaimed water is 14.1¢/1000 gallons, while reclaimed water from an IPCT plant is only 5.9¢/1000 gallons (1.2 kopecks/cu m).

In summary, the use of IPCT equipment and technology should be considered thoroughly for its long term investment advantages against the backdrop of the 1983 and 1985 requirements. The advantages of IPCT are the following:

1. Economically competitive with biological treatment systems for 1977 standards.

2. Upgradable to 1983 standards more economically than the addition of tertiary treatment to biological systems at lower overall costs.

3. Helps local, state and federal governments reduce the economic dislocations of catch-up investment cost now facing many communities for high quality treatment.

*4. Decomposes PCBs (polychlorinated biphenyls).

*5. Decomposes pesticides – DDT, 2, 4, 5-T.

*6. Produces ash product-fertilizer plus has several possible other uses.

7. Controls heavy metals (4, 8).

8. Reclaims energy from sludge which saves both fuel and money.

9. Meets EPA air pollution standards – particulates.

10. Recognized as an insignificant source of air pollution by the San Francisco Bay Area Air Pollution Control District.

Clearly, as the USSR and the US move to higher quality levels in both the air and water sectors, the overall environmental impact of technology must be considered. Accordingly, advanced IPCT and thermal processing technology deserve to be fully analyzed for their resource recovery and purification benefits, as well as for their "disposal" and cost savings benefits. IPCT processes appear as the logical choice, where the influent is applicable, as the eventual expenses of upgrading secondary treatment level IPCT systems are considerably less than upgrading biological treatment facilities to tertiary treatment. The environmental impacts of waste streams from recalcination, carbon regeneration and other processing systems utilizing multiple hearth furnaces are negligible, while recovering valuable resources – lime, energy, carbon and plant nutrients. It could be noted that in urban centers where disposal of large sludge quantities has become a real problem, reclamation/incineration processes offer cost/benefit advantages for both IPCT and biological treatment.

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*These benefits could also be received in biological treatment plants having multiple hearth furnaces.

PROCESSING AND NEUTRALIZATION OF INDUSTRIAL WASTES FROM IRON AND STEEL EFFLUENTS TREATMENT

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VNIPIChermetenergoochistka

The iron and steel enterprises effluents contain some contaminants which are specific for the branch of industry. The contaminants may be subdivided into 3 groups: soluble and insoluble mineral and organic compounds.

During the effluent treatment and the stabilization of water supply systems the following waste materials are formed – sludges, high mineralized effluents and wastes with organic compounds.

Sludges

The iron and steel plant sludges may be divided as follows:

–iron containing sludges. The group involves mill scale, sludges from the gas cleaning of sintering, blast furnace, open hearth, converter and electric steel plants;

–gypsum containing sludges. They include sludges. They include sludges which are formed in the lime gas desulphuration process in the neutralization process of the effluents containing sulphur oxides;

–others. They involve treatment products formed in small quantities: sludges from casting machines, ferro-alloy furnace gas cleaning plants, scarfing machines etc.

The materials ratio is as follows.

Iron containing sludges including:	– 89,16%
a/ sintering plants	– 32,50%
b/ blast furnace stockhouse	– 10,83%
c/ blast furnace gas cleaning plants	– 19,17%
d/ open hearth furnace gas cleaning plants	– 3,16%
e/ converter gas cleaning	– 3,00%
f/ electric furnace gas cleaning plants	– 0,50%
g/ mill scale	– 20,00%
Gypsum containing sludges including:	– 6,67%
– desulphuration sludges	– 2,5%
– sludges from neutralized sulphur effluents	4,17%
Other sludges and dusts	– 4,17%
TOTAL	– 100%

Sintering plant sludges

Up to 90 - 95% sludges are formed in sintering housings during hydraulic blasting of gas collectors filter bags, fan system collectors during hydraulic cleaning of rooms and pipelines from dry and wet cleaning units for waste gases and fan systems.

The remaining 5-10% sludges come from other sintering plant departments: charge treatment housing, lime calcination housing, stock yards, car dumpers and so on. The main sources of their formation are fan systems and charge materials falls. The sludges from equipment and pipelines washing as well as sludges from hydraulic rooms cleaning are supplied at a time and irregularly.

Great bulk of sludges consists of sinter particles as well as raw materials: ore, coke, coal, limestone. As a rule sintering plants products are of rather coarse size distribution. Sludges from dust bags of gas collectors and hydraulic cleaning include 60-65% particles > 0,3 mm, from installations for dry and wet cleaning up to 10% particles > 0,3 mm, the greatest part of fines is in the sludges from fans.

All sludges contain a large quantity (26 to 36%) of particles sizes of which are 0,15-0,05 mm. Some sludges have a lot of particles < 0,005 mm, and it may be accounted for more efficient cleaning process of waste gases. Solid phase density of sludges from sintering plants is 3 to 4 g/cm^3.

Sludges from stock houses of blast furnace shops

Sources of sludges formation are falls from conveying and production equipment; dust deposition on building and equipment elements, as well as dust from wet and dry air cleaning systems.

Composition of sludges from stock houses is similar to those from sintering plants and gas cleaning installations of blast furnaces. As to the particles size they may be classified as coarse-sized ones (up to 60% particles of 0,01-0,05 mm size). Solid phase density of sludges from the under-bins premises is from 3,9 to 4,2 g/cm^3.

Sludges from gas cleaning installations of blast furnaces

Sludges are formed during the scrubbing of blast furnace gases and they are a mixture of fine particles of the ore, fluxes, coke, entrained from the blast furnace by the gas stream. Passing through a reducing zone of the furnace they are partially reduced and partially oxidized and combine. As a result of it sludges contain primary ore elements and new compounds created in the blast furnace.

Size distribution of sludges from the gas cleaning plants of blast furnaces is similar to the size distribution of sintering plants sludges and in some cases at the high efficiency of blast furnace gases in dry dust catchers, their particles are similar.

As to the chemical composition sludges of effluents from gas cleaning installations of blast furnaces, especially coarse-sized are also similar to sintering plants sludges. Fines contain a smaller amount of iron compounds and a greater amount of silicon oxides. Solid phase density of sludges from gas cleaning installations of blast furnaces is 2,2 to 4 g/cm^3.

Sludges from gas cleaning installations of converter and open hearth furnaces shops

Sludges include the finest particles of oxides of iron, aluminum, calcium, manganese and other elements. The main component consists of iron oxides. As to the structure the particles are regular spheres of different sizes coated with a thin reddish crust. Size distribution of sludges is mainly presented by the finest particles with a diameter 0 to 50 . Density of a solid part of sludges from the gas cleaning installations of converter is 3,3 to 4,4 g/cm3, of open hearth shops – 4,3 to 4,9 g/cm3 due to a high iron content in sludges.

Sludges from gas cleaning plants of electric melting furnaces

Sludge composition depends on the charge ratio or on kinds of the output being melted grade of steel, type of alloy). Sludges include a relatively large quantity of iron compounds /30 to 40%/, as well as of heavy and non-ferrous metals (chrome, nickel, manganese, magnesium). In some sludges chrome content may reach 10%, nickel - 8%, manganese – 7%, magnesium – 20%. Sludges may also include titanium, tungstem, vanadium and other elements. As to their particles size these sludges are similar to sludges from the gas cleaning of converter and open hearth furnace shops. Solid phase density in these sludges makes up 2 to 4 g/cm3.

Mill scale

The sludge consists of iron oxides with content 33,0 to 65,0% FeO and 63,0 to 27,0% Fe_2O_3. In addition to the solid phase the scale comprises 5 to 20% oil. Mill rolls, rollers, roll tables, hot and cold saws cooling water, descaling and roll table pit washing wastes are contaminated with scale and lubricating oils. The scale content of wastes is 2 to 4% rolled metal weight. Scale falling under mill and roll tables is conveyed to a primary settling basin which is a scale pit for settling 80 to 85% coarse scale.

Preliminary clarified waste waters are directed by gravity from the primary settling basin to a secondary one where fine scale is settled in quantity about 10% coarse one.

The scale is classified to coarse (>10mm), intermediate which is washed out from a pit under the mill and brought away along channel bottom (10mm and less) and fine (<2mm). The amount of intermediate and fine scale varies depending on mill type and rolled metal grade.

Scale solid phase density is 5,15 to 5,0 g/cm^3.

Desulphuration sludge

The sludge forms in the process of wet limestone scrubbing of sintering off-gases.

It consists principally from calcium carbonate and sulphite.

Sludge particle size distribution varies greatly and is a function of limestone grinding fineness while a desulphuration suspension preparing. The sludge solid phase density is 2,6 to 2,7 g/cm^3.

Neutralized sulphuric acid waste sludge

The sludge forms while neutralizing waste pickling liquors and pickling line washing waters. The wastes are usually neutralized with lime suspension. The neutralizing precipitates contain principally gypsum and iron hydrooxides. The sludge solids are very dispersed and precipitated with great difficulty.

Other sludges

The sludges form in very small amounts, and their utilization is not a serious problem in comparison with a total volume of all solid wastes through utilization methods are required to be determined in every concrete circumstances for these wastes too.

HIGH-MINERALIZED WASTE WATERS

These wastes include neutralized washing waters and waste pickling liquors, regeneration and washing waters of reagent water treating systems, recirculation system blowing-down waters from metal working process and wet gas cleaning units. The wastes are characterized by multicomponent salt composition and salt content exceeding sanitary standards. The most of these waters are saturated with $CaSO_4$. The total amount of the waste waters to be neutralized at steel or metal working plants can approach 500 m^3/h.

ORGANIC WASTES

Waste rolling oils

The wastes form while treating or decomposing lubricating and cooling emulsions. The lubricating and cooling emulsion treating oil wastes contain 20 to 50% water and up to 10% mechanical impurities. Oil wastes that are formed while decomposing an emulsion after clarifying contain up to 5% water and about 3%

mechanical impurities. The impurities consist mainly from fine iron oxides. Oil waste specific yield is 0,5 to 1,5 kg/t rolled product.

Waste decreasing solutions

The wastes include emulsified oils, anorganic detergents (Na_2CO_3, NaOH, Na_3PO_4 etc) as well as different surfactants. There are up to 0,5% oil, up to 100 g/l anorganic detergents, up to 1% surfactants. The waste degreasing solutions yield approaches 3-5 m /h at an intermediate capacity metal working plant.

WASTES UTILIZATION, TREATMENT AND NEUTRALIZATION

Sludges

Iron containing sludges can be utilized in sintering, blast-furnace and steel production processes according to wastes composition. They can be used at sintering plants without any preliminary pelletizing and at others in briquettes or pellet form. The iron containing sludges dumping together with other sludges in settling pond as practicized at some mainly old works results in metal losses and surrounding pollution. Therefore modern steel plants are commissioned in conjunction with iron containing sludges treatment and utilization systems.

According to references a total utilized iron containing sludges amount is now about 63.0%. The sludges are used the most successfully at sintering plants. The most of them are the same plants sludges. Sometimes they include also steel production and seldom blast furnaces gas cleaning systems sludges.

The sludges using without any special dewatering units is hindered because their high humidity makes their conveyance difficult, results in the plant site, equipment and hall pollution. A preliminary preparing operation in special units (dewatering and drying) is necessary as well while utilizing steel production gas cleaning systems sludges in pelletized form (as briquettes or pellets) in blast-furnace and steel production processes.

Gypsum containing sludges can be efficiently utilized to reclaim and fertilize acid soils. The studies performed have shown corn crops to increase by 25 to 50% as a result of desulphuration systems and sulphuric acid liquors neutralization units sludges applying in amount of 4 to 5 t per ha.

The sludges must be dewatered to 6 to 8% humidity before being applied. They can be utilized also as a base for a constructional 250-350 grade cement and further for constructional concretes and elements.

Thus, a prinicpal condition of successful sludge utilization is special dewatering (preparing) systems development.

Sludges dewatering equipment and methods

Sludges dewatering units are following: classifiers, vacuum filters, press filters, centrifuges.

Classifiers. They are used to classify multisized suspension solids with size up to 1 to 5 mm into 2 or more fractions. The classifiers can be of two main types: settling or centrifugal units. As to settling classifiers horizontal clarifiers, spiral and elevator classifiers are put in practice to dewater waste water sludges. Out of centrifugal classifiers bent sieves or conical screens, hydrocyclones and settling centrifuges are employed.

Horizontal clarifiers are the simplest classifiers. They are put in rather wide practice of metallurgical waste treatment. The clarifiers are not quite efficient. A fault of them is low sludge dewatering rate.

Because of relatively low classification rate, poor discharge mechanization and small dewatering rate the clarifiers are designed no longer but are to be replaced by more perfect equipment.

Spiral classifiers. These devices have been used for a long time in ore-treating industry. They are more widely spread in the sludge dewatering practice of metallurgical plants than all the other types of mechanical classifiers.

In designs of batch produced spiral classifiers, bath and conveyer parameters are chosen according to the working conditions on ore pulps, which as a rule contain a considerable amount of solid phase. However, in the conditions of dewatering units treating metallurgical plant sludges, considerably diluted suspensions are mostly supplied to the classification. The adopted relations of bath and discharging conveyer parameters of batch designs are not optimal in this case.

Due to this fact one should reconstruct spiral classifier baths to increase the drainage loading.

Elevator classifiers or dredging sumps.

These devices are taken from coal concentration industry. The design is quite simple – they consist of sump, in which the dewatering elevator boot is placed for sedimented sludge output. Their operation on metallurgical plant sludges is not practically investigated. The loadings are taken on analogy with those on coal concentration plants, though the difference in working conditions is even more in this case then in previously discussed one with spiral classifiers.

Bent and conical sieves are also taken from coal concentration field. These units are characterized by simple design, high production rate and operational reliability. Yet they are rarely used in sludge dewatering practice of treating metallurgical plant wastes, but seem quite promising.

Hydrocyclones are widely used in water treatment and sludge dewatering practice. Design methods applied to different types of ore sludges are available. As for metallurgical plant sludges, these methods need some specifications.

Bowl centrifuges are often treated as dewatering equipment not of classifying type, though practically they are classifiers, because of quite low meaning of boundary grain size and that is why they will be discussed later on.

Vacuum filters. Band, disk and drum vacuum filters are used in the precipitate treatment of metallurgical plant.

Band vacuum filters are used for coarse sludge dewatering as well as for not-classified sludge, when the unit production rate is low. Both band and drum vacuum filters are characterized by small filtering surface per unit of area occupied.

Disk vacuum filters are used for sludge dewatering with size 0,3 to 0,1 mm from gas cleaning units of sintering, blast furnace and converter processes. They are most widely spread than other types of filters.

Drum vacuum filters are used in the same cases as the disk ones. In our country drum filters are relatively rare.

Press filters. In practice of waste water precipitate treatment of metallurgical plants press filters are applied to dewatering of precipitates which are hard to dewater (sludges of open-hearth gas cleaning units; sulphuric acid liquor neutralization sludges, etc)

High classifying rate is guaranteed: the precipitate contains a minimum quantity of moisture, and the filtrate is of maximum purity. Press filters have relatively simple design, highly developed filtering surface per unit of occupied area and allow to use high pressure drop that is especially important when dewatering suspensions with high-dispersed solid phase.

In practice of precipitate dewatering of metallurgical plant waste waters automatic chamber type press filters with plate clam of FPACM type (institute UkrNIIChimmash and Berdichev chemical machine works "Progress" design) got some spreading.

Press filters are produced with filtering surface of 2,5; 5; 10; 25 and 50 m^2. FPACM press filter metal consumption per weight unit of filtered products is 2-3 times lower than that of frame press filters, and production rate is 4-6 times higher. All the filtering processes are automatized.

Centrifuges. Centrifuges are not widely spread in the practice of waste water precipitate treatment at metallurgical plants in our country.

At present investigations are carried out on application of bowl centrifuges with screw discharge conveyor for dewatering different sludges.

Application – of such equipment provides considerable simplification of sludge dewatering methods, as it allows to reduce a number of equipment units and dewatering units room volume.

Process flow diagrams. Conditionally one can distinguish three types of process flow diagrams:

1) for multisized sludge dewatering

2) for dewatering of monodispersed sludge of intermediate size

3) for high dispersed sludge dewatering.

The first type is characterized by sludge classification to 2-3 fractions, each of them is dewatered separately on its type of equipment.

Usually the largest fraction is dewatered in classifiers, the fraction of intermediate size – in band vacuum filters and the finest fraction in disk or drum vacuum filters. Sometimes both intermediate and fine fractions are dewatered together in disk or drum vacuum filters.

The second type diagram is widely used for dewatering of converter gas cleaning units sludge, and includes disk and drum vacuum filters as dewatering devices. The third type can be used for dewatering of open hearth and electromelting furnaces gas cleaning units sludges and for neutralized sulphuric acid sludge; it is characterized by press filter application.

Equipment operational parameters depend on physical and mechanical properties of suspension being dewatered.

For the present a considerable number of studies on operational parameters of vacuum filters, press filters, centrifuges and classifiers for different sludges has been carried out.

Investigations on sintering sludge dewatering resulted in determining band and disk vacuum filters operational parameters. For band vacuum filters while dewatering +0,25(0,3) mm sintering sludge with primary pulp concentration 400-600 g/1, it is recommended loading of 4,0 to 5,0 t/m2 h and dewatered precipitate moisture - 13 to 15%.

For disk vacuum filters loadings are maintained in dependence of feeding – 30 fraction content with concentration of solids 400 g/1.

Table 1

Specific production rate of disk vacuum filters versus size distribution of solids in feeding.

Specific production rate kg/m2 h while concentration of solids in feeding is 400 g/l	30 u fraction content in filter feeding, %
450	10
400	20
320	30
250	40
150	50
100	60

Following correction factors taking into account the concentration are introduced: 500 g/l – 1,05; 600 g/l - 1,30; 700 g/l – 1,65; 800 g/l – 2,20; 900 g/l – 2,60.

Dewatered pricipitate humidity after disk vacuum filters depends upon the solid phase granulometric composition, used vacuum rate, precipitate depth and other factors. It may vary within close range 18 to 22%.

While dewatering converter gas cleaning system sludge production rate of disk vacuum filters is 0,07 to 0,1 t/m2/h, dewatered sludge humidity is within range 27 to 35%. Due to rather high humidity dewatered converter sludge is usually subjected to thermal drying after vacuum filters.

While dewatering sludge formed in sintering plants limestone gas desulphuration process on vacuum filters following data were obtained: unit load – 50 – 125 kg/m2h (corresponding to concentration extreme values of initial suspension 100 – 500 kg/m2h), precipitate humidity 28 to 30%.

Conditions of press filters working on various types of precipitates were investigated. The studies were carried out on sludge of open hearth, converter and electric steel furnace gas cleaning systems, on desulphuration units sludge of sintering plants and also on sludge obtained while neutralizing sulphur acid effluents. Table 2 illustrates data on dewatering of open hearth, converter and electric steel furnace gas cleaning systems sludges from different plants.

Press filter production rate depending upon physical and mechanical sludge properties, pulp concentration and cycle characteristic was within range 40 to 95 kg/m2h at precipitate humidity – 14 to 33%.

In experiments with dewatering of sludge, formed in the limestone gas cleaning desulphuration process, specific production rate on press filters FPACM was 150 to 330 kg/m2h (corresponding to concentration extreme values of initial suspension – 150 to 400 g/l) and dewatered precipitate humidity – 15 to 18%.

While dewatering sludge formed as a result of sulphuric acid waste neutralization by lime milk specific production rate of press filters was 5 to 12 kg/m2h at solid content in initial pulp 1,5 to 5% respectively and

Table 2

Data on dewatering of sludge from steel furnaces gas-cleaning system on filter-press ФПКМ -0,5

Type of sludge	Solid phase content in suspension, g/l	Working pressure, atm	Cycle characteristic			Obtained data			
			total duration. min	filtration time, min	precipitate drying time, min	precipitate depth, mm	precipitate humidity, %	filtrate solid content, g/l	specific production rate, kg/m² h
1	2	3	4	5	6	7	8	9	10
Open-hearth gas-cleaning system (plant A)	450–470	4.0	8	3	3	4–5	17–18	up to 4	60–70
Open-hearth gas-cleaning system (plant B)	270–300	4.5	16	12	2	6–7	20–20.5	up to 3	40–45
Open-hearth gas-cleaning system (plant D)	250–280	4.0	8	4	2	4–5	19–20	up to 3	55–60
Converter gas-cleaning system (plant A)	360–380	5.0	14	10	2	10–12	32–33	up to 3	60–65
Converter gas-cleaning system (plant B)	250–270	4.0	15	11	2	6–7	19–20	up to 3	50–55
Converter gas-cleaning system (plant C)	330–350	4.0	10	6	2	11–12	25–26	up to 3	90–95
Electric steel furnace gas-cleaning system (plant A)	270–300	4.0	18	13	3	4–5	14–15	up to 4	45–50
Electric steel furnace gas-cleaning system (plant B)	370–400	4.0	9	5	2	10–11	29–30	up to 3	75–80
Electric steel furnace gas-cleaning system (plant C)	240–260	4.0	7	3	2	8–9	21–22	up to 4	75–80

precipitate humidity was 58 to 61%.

It was stated that in addition to physical and mechanical solid properties the production rate of press filters used for dewatering of hot rolling mills scale in secondary settling basins is greatly influenced by oil content in pulp. Thus at a plant in a process of dewatering scale containing 20% oil (in reference to oiled solids) specific production rate on press filters FPACM was 10 to 25 kg/m2 h (at solid concentration 140 to 550 g/1 respectively) while at another plant with the same concentrations of scale, containing 8% oil, specific production rate was about 25 to 75 kg/m2h.

Filtration of oiled pulp was shown to be greatly improved by addition of lime milk. While dewatering the said scale containing 20% oil lime addition to the pulp in theoretical amount of 2 g CaO/1 resulted in 2,5 – 3 times increase of specific production rate. The lime addition did not influence greatly on precipitate humidity which was within range 10 to 12%.

Under relatively small oil content in scale (up to 10%) the lime addition influence much less on production rate.

Both dewatering and deoiling are the aim of the process of scale treatment before utilization. However, filtration process cannot provide effective oil separation since oil passing through precipitate filter layer is adsorbed on solid phase particle surface, as a result of which process its considerable part is left in precipitate.

With the aim of searching out more effective methods of such a sludge treatment the dewatering and deoiling processes of the secondary settling basin scale in bowl centrifuges with screw conveyer discharge of sludge were studied. These studies showed that as to deoiling the centrifugation process in bowl centrifuge has a considerable advantage in comparison with the filtration process, especially for the scale with the great oil content.

These studies were carried in full-scale centrifuge of NOGSh-32S type. The centrifuge throughput on pulp was 2.5 to 4.0 m^3/h with the solids content 50 to 350 g/1.

The humidity of dewatered precipitate was in the range of 10 to 20%, and the oil content in the range of 2 to 5%.

The using of bowl centrifuges may be also very promising for treatment of the other precipitates. However, it requires the carrying out of definite studies connected with finishing and putting into the practice of this equipment.

In conclusion it should be noted that in present some decisions on process flow diagrams of main steel plants sludges dewatering are available and this does not hinder putting into practice modern dewatering units. The main factor decelerating the construction of these plants are too slow rates of construction, although namely these plants are one of the important resources of raw material utilizing methods improving in steel-making industry.

HIGH MINERALIZED WASTES

One of the main trends in high mineralized wastes neutralization is thermal desalting. The wastes desalting problem is the complex of problems connected with high concentration, obtaining of dry salts, their utilization and storage.

The most of steel plants wastes are saturated with components capable to form the scale on the heating surfaces, that is why the main difficulties while high concentrating such wastes are connected with the control of scale formation.

In present, in steel-making industry one pilot plant for thermal desalting is operated with production rate 100 m^3/h. For high concentrating scale-forming wastes tubular vaporizers with forced circulation are applied.

Studies data and plants operation practice for sea water desalting show the following types of wastes deep concentrating plants are the most reasonable.

1. Vaporizers with adiabatic evaporators and heating of evaporating water in contact heaters with water-repellent or gaseous heat-transfer agent.

2. Vaporizers with tubular evaporators and preliminary softening of water by thermal and reagent methods.

For small production rate plants vaporizers consisting of two or three tubular devices with forced circulation of water concentrated by evaporation.

In present, two types of vaporizers for high concentrating and drying of drop-forming wastes have been developed. Multibodied vaporizer with tubular evaporators and thermal softening of initial water which is to be constructed at one of the Ural plants, as well as a multibodied plant with adiabatic evaporators and heating of water concentrated by evaporation in contact device with water-repellent heat-transfer agent is also to be constructed at one of the Ukraine plants.

The still residue drying at these plants is provided for in fluidized bed furnaces.

The problems of salt utilization are being studied in laboratory conditions.

WASTES WITH ORGANIC COMPOUND CONTENT

One of the main methods of liquid wastes neutralization containing organic compounds in different branches of the USSR industry is flame method. Lately, the most widespreaded agregates for flame neutralization are cyclone furnaces.

For burning of oil wastes and for waste degreasing solutions flame neutralization the cyclone furnaces of different production rate have been developed. The cyclone type devices are being constructed at some steel-making and metal working plants. They are characterized by high specific parameters. Volume specific intencity when burning oil wastes is about 5.10^6 kcal/m^3h. Volume specific loading while solution neutralizating is approximately 1 t/m^3h.

FUNDAMENTAL PRINCIPLES OF SELECTING THE METHOD FOR PROCESSING SEWAGE SEDIMENTS IN ACCORDANCE WITH THEIR PROPERTIES

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I.S. Turovsky, Cand.Sc. (Eng.), Head of Sediment Treatment and Utilization.

One of the most intricate problems associated with protection of water reservoirs from pollution is the treatment of the sediment.

Sewage sediments belong to the class of hard-to-filter silt suspensions, their treatment is complicated by their large size and high humidity.

The sediment treatment methods include fermentation in anaerobic and aerobic conditions, drying on silt pads and ponds; dehydration on vacuum filters, centrifuges, filter presses and other devices, and decontamination by thermal treatment or incineration.

Silty pads and silt ponds, which are widely used for drying sediments, are extremely inefficient and occupy large areas in city outskirts.

The use of mechanical dehydration makes it possible to considerably reduce the areas and time required for sediment drying, with simultaneous mechanization and automation of the process.

Mechanical dehydration can be applied both to fermented and unfermented sediments.

Among the methods for mechanical dehydration, drum-type vacuum filters are most widely used.

The capacity of vacuum filters depends on the composition and properties of the sediments, the ratio between the sediment from the primary settlers and active silt in the mixture, and also on the methods for preparation of the sediments for dehydration. Of great importance is the composition of the sewage under treatment. All these factors differ from aeration station to another.

The extent of water removal from the sediment is indicated by the specific resistance of the sediment to filtration.

The specific resistance of a sediment is found from the formula.

$$r = \frac{2PF^2}{\eta \cdot c} b \qquad 1$$

where:

r is the specific resistance of the sediment,
is the pressure (vacuum),
F is the filtering area,
is the filtrate viscosity,
c is the concentration of dry matter in the sediment,
$b = \frac{\tau}{v^2}$ is a parameter characterizing water removal from the sediment,
τ is the filtering time after the pressure was set up,
v is the filtrate volume obtained after a constant pressure was set up.

In determining the specific resistance of the sediment the parameter "b" can be obtained experimentally, while the value of "r" can be calculated from Eq.(1) /1/.

The specific resistance of sediments at city aeration stations varies widely. An analysis of specific resistance values shows that unfermented sediments in primary settlers and uncompacted active silt have a much lower specific resistance than fermented sediments.

A sediment fermented in thermophilic conditions has the highest specific resistance. It has also been established that the higher the specific resistance, the lower is the capacity of the vacuum-filters and the more thorough the treatment which must be undergone by the sediment prior to mechanical dehydration. /1/.

Calculation formulas have been proposed which enable one to determine the amount of eater necessary for washing the fermented sediments, the doze of the chemical reagents required for sediment coagulation, the expected capacity of the vacuum filters, and also the optimum conditions of their operation /2/.

The specific resistance of the fermented particles by washing with water or purified sewage. The curves of reduction in the specific resistance of the fermented sediments in the course of their washing can be approximated by the equation

$$\lg R_n = \lg R_0 \cdot e^{-an}, \qquad 2$$

where:

$R_0 = r_0 \cdot 10^{-10}$ is the specific resistance of the washed sediment, cm/g;
$R_n = r_n \cdot 10^{-10}$ is the specific resistance of the washed sediment, cm/g;
n = is the amount of washing water, cu m per 1 cu m sediment;
a = is a coefficient depending on the concentration of the initial and washed sediment, the removal of the suspended matter with the drain water, and other factors, which varies within the range from 0.04 to 0.14.

The filtering devices show stable operation when the specific resistance of the sediments reduces from the initial value to (5 - 50 x 10^{10} cm/g, respectively. For most sediments, the above reduction is achieved by coagulation or flocculation with the aid of chemical reagents.

The optimum dose of reagents is established from the curves of reduction in the specific resistance of the sediment during experimental coagulation with different doses.

The reagent dose can be tentatively determined from the formula:

$$D = k\left(\sqrt{R} + \sqrt{\frac{h}{c} \cdot 0.001 \text{ alk}}\right), \qquad 3$$

where:

D is the reagent dose in per cent of the sediment dry weight;

R $r \cdot 10^{-10}$ is the sediment specific resistance, cm/g;

h is the sediment humidity, %;

c is the concentration of the sediment dry matter, %;

alk is the sediment alkalinity, mg/l;

k is a coefficient depending on the type and chemical composition of the reagent used.

The efficiency of the drum-type filters is determined from the formula:

$$L = 0.24 \frac{100 - hd}{hi - hd} \sqrt{\frac{\rho \cdot m \cdot P(100 - hi)}{\eta \cdot M \cdot R}} \qquad 4$$

where:

L is the vacuum filter capacity, kg/m^2 per hour, with reference to the sediment dry matter;

hi hd is the humidity of the initial and dehydrated sediment, respectively, %

ρ is the density of the initial sediment, t/m^3;

m is the duration of the vacuum effect in relation to the total filtering cycle, %;

P is the working vacuum, mm Hg;

η is the filtrate viscosity, cp;

M is the drum revolution time, min.

Slimes with a low specific resistance often do not require any treatment prior to dehydration. They can also be used for reducing the specific resistance of sediments in city sewage. In particular, such slimes include products of neutralization of sulphuric-acid – containing etching solution with lime, and waste from some industrial enterprises.

When choosing the sediment treatment method, a study into the mechanism of binding of the water the solid particles of the sediment is of considerable importance as well as specific resistance evaluation /2/.

From the classification of the types of water binding proposed by Rebinder it follows that breaking of the water-solid bonds requires the expenditure of a definite energy. The vacuum at which the sediments are dehydrated on the vacuum filters equals 400 to 500 mm Hg. The theoretical limit for water removal by vacuum filtering is the water content of microcappilaries with a radius of not less than 0.005 mm. Filter pressing or centrifuging during which higher pressures are developed removes a greater amount of water from the sediments, and the filtered sediment has a lower water content as compared with vacuum filtering. The maximum amount of water removed from the sediments by mechanical dehydration is characterized by the position of the first critical humidity point (Fig. 1) and depends on the type of sediment and the degree of its readiness for mechanical dehydration.

It can be seen from the figure that compacted active silt contains more hard-to-remove water than a fermented sediment, while the latter contains more such water than the unfermented sediment from the primary settlers.

The water content of the active silt on section b,c reduces from 98 to 87.5%, that of the fermented mixture, from 97.5 to 84.6%, and that of the unfermented sediment from the primary settlera, from 94.6 to 73%.

When sediments are coagulated with chemical reagents, part of the water bound by the physicomechanical and physicochemical bond is released and the amount of adsorption-bound water is reduced. The value of the first critical point decreases as well.

Aeration stations with a capacity of up to 50 thous. m^3/day use the sediment centrifuging method.

Centrifuging can be effected either with or without the use of chemical reagents. A disadvantage of this method, which limits the scope of its application, is the large amount of suspended solid carried away with the fugate.

The efficiency of retention of the sediment dry matter during centrifuging is determined from the formula

$$\varepsilon = \frac{C_c\,(C_{sed} - C_f)}{C_{sed}\,(C_c - C_f)} \cdot 100\%, \qquad 5$$

where: C_{sed}, C_c and C_f are, respectively, the concentrations of the initial sediment, the cake, and the fugate.

Investigations show that in approximate calculation of the dry matter retention efficiency one can use data obtained on laboratory cup centrifuges.

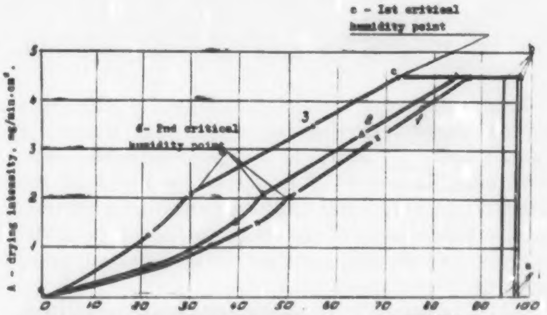


Fig.I.Curves of sediment drying intensity.

1- compacted active silt
2- fermented sediment
3- unfermented sediment.

The centrifuge capa city index is expressed by the relation

$$E = F \cdot S, m^2, \qquad 6$$

where:

F is the surface area of the centrifuge draining cylinder;
S is the separation factor.

$$S = \frac{W^2 \cdot R}{g} \qquad 7$$

where:

W is the rotor angular radius, m;
R is the rotor radius, m;
g is the gravity acceleration, m/sec^2.

In order to determine the type and size of the centrifuge, one can change the surface area of the draining cylinder by varying the diameter of the draining orifice only within a small range, whereas the separation factor can be varied up to 2000-3500 for the same machine.

The sediment residence time in the rotor of an industrial centrifuge, which depends on the capacity index, is changed mainly by regulating the centrifuge capacity. Hence, the principal parameters to be determined when simulating the process is the separation factor and the centrifuging time. The effect of the separation factor and centrifuging time on the efficiency of sediment separation is easily determined on a laboratory-type cup centrifuge.

A comparison of the results of experiments on a laboratory and an industrial centrifuge suggested a method for tentative estimation on the dry matter retention efficiency with an industrial centrifuge from laboratory data with the use of the "centrifuging index" proposed by us /3/:

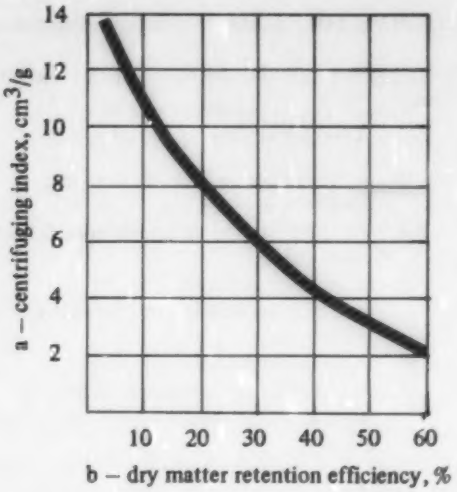
$$C_I = \frac{V}{V_0 C} \cdot 1000\, cm^3/g \qquad 8$$

where:

V is the volume of the compacted sediment, cm^3,
V_0 is the volume of the initial sediment, cm^3,
C is the concentration of the initial sediment, g/1.

The results of the experiments carried out on a laboratory-type centrifuge show that the process of separation of all types of sediment is stable when centrifuging lasts over 2 min and the speed of the centrifuge rotor is 6000 rpm; the centrifuging index is actually independent of the concentration of the initial sediment and remains constant for a definite type of sediment.

Based on the data obtained with a laboratory-type centrifuge -3 and an industrial centrifuge HO -325, we derived the dependence of the sediment dry matter retention efficiency on the centrifuging index (Fig. 2), which is approximated by the expression:



$$\mathcal{E} = 115 \cdot e^{-0.224 C_I} - 19 \cdot e^{-0.44 C_I} \qquad 9$$

The use of the centrifuging index as a criterion enables one to estimate the increase in dry matter retention efficiency in preliminary treatment of sediments with chemical reagents, by freezing and thawing, heating, prolonged aeration, etc.

Mechanically dehydrated sediments belong to the group of paste-like, colloidal, capillary-porous bodies whose intensive drying involves difficulties.

Investigations on thermal drying of sediments dehydrated on vacuum filters, filter presses, and centrifuges show that the drying curves have the same shape for different types of sediment and differ only in the position of the critical points, which mainly depends on the initial water content of the sediments (Fig. 3). Sediments are dried in two stages, at a constant (period I) and a reducing (period II) velocity.

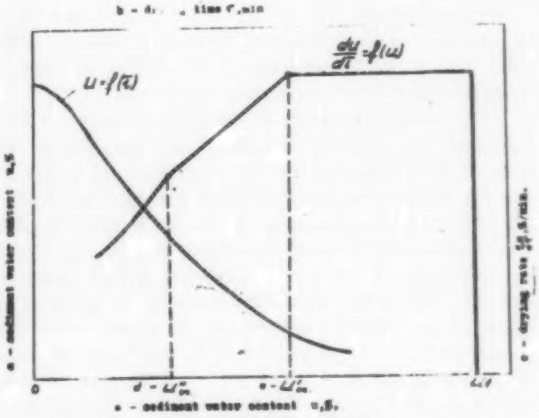


Fig.3. Drying kinetics of dehydrated sediments.

In the first stage the drying rate depends on the conditions of external mass- and heat-exchange between the surface of the material and the drying agent. In the second stage the drying rate depends on the conditions of redistribution of humidity and heat inside the layer of material.

To avoid overdrying of the surface layer, the rate of evaporation must correspond to the moisture diffusion from the inside of the material.

When intensive drying regimes are used, with high velocities and temperatures of the drying agent (which is typical of the drying of sediments in the suspended state), the first drying stage considerably reduces. For materials which dry like sediments with the formation of a dry crust on the surface it is advisable to resume the constant-drying-rate stage by breaking the crust and thereby exposing the humid surfaces. This kind of regime is achieved by drying in gas suspension counter-currents /4/.

Treatment of experimental data in criterial dependence $Nu_{ef} = f(Re)$ shows that the experimental data are correlated by the formula $Nu_{ef} = 9.5 \times 10^{-3} Re$ within the range $200 < Re < 500$.

To complete sediment drying in the second stage it is expedient to use the air fountain regime.

Conclusions

1. The main factors characterizing water removal from sewage sediments are the specific resistance of the filtration sediment, the centrifuging index, and the position of the first critical humidity point.

2. Some relations are recommended which make it possible to select the sediment treatment method and determine the degree of its readiness for mechanical dehydration and also the operating conditions of the filtering devices according to the value of the specific resistance of the sediment, the centrifuging index, and the critical points of the water-solid bond.

3. The most efficient technique for thermal drying of dehydrated sewage sediments is the method of gas suspension counter-currents coupled with the air fountain regime.

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CAPTIONS TO FIGURES

Fig. 1 Curves of sediment drying intensity: 1-compacted active silt; 2-fermented sediment; 3-unfermented sediment; c-1st critical humidity point; d-2nd critical humidity point; A-drying intensity, mg/min.cm^2; B-humidity, %.

Fig. 2 Dependence of dry matter retention efficiency on centrifuging index in sediment dehydration on centrifuge HOГΨ-325 with Q=3 - 4 m^3/hr: a-centrifuging index, cm^3/g; b-dry matter retention efficiency, %.

Fig. 3 Drying kinetics of dehydrated sediments: a-sediment water content u, %; b-drying time τ, min; c-drying rate $\frac{du}{d\tau}$, % 5/min; d-u''_{cr}; e-u'_{cr}.

PROTOCOL

of the second Meeting of the USA and USSR delegations
on the problem of prevention of Water Pollution from
industrial and Municipal Sources
(Cincinnati, USA, November 9-23, 1975)

Between November 9-23 the Meeting of the USA-USSR delegations on the problem of waste water treatment took place.

The American delegation was led by Mr. Harold P. Cahill, Jr., Director of Municipal Construction Division, US Environmental Protection Agency.

The Soviet delegation was led by R.F. Slavolyubov, Chief of the Glavpromstroi Proyekt Department, Gosstroi USSR.

The list of participants is attached in Appendix 1.

In the course of the meeting the following was accomplished:

1. A symposium on physical-chemical treatment of waste waters.
2. The accomplishments of the 1975 program of cooperation were discussed.
3. Coordination of the Working Program for 1976.

I

At the Symposium 16 reports devoted to the problems of physical-chemical waste water treatment were delivered: the US delegation delivered 9 reports; the Soviet delegation 7 reports.

The list of reports delivered is attached as Appendix II.

Of particular interest were papers by Soviet specialists on new polyelectrolytes and on waste water treatment from concentrated oil and emulsion, and reports of American specialists on activated carbon absorbtion waste water treatment and on physical-chemical with utilization of coagulants.

The delegations have agreed that each side will publish all reports presented at the Symposium in the necessary number of copies in its own language prior to May 1, 1976, and will distribute them among interested organizations.

II

Concerning the results of the 1975 program of cooperation, the following was noted:

The sides discussed twice the results of current research, exchanged scientific and technical literature and carried out two US-USSR symposia on sludge management (USSR, Moscow, May 1975) and on physical-chemical waste water treatment (USA, Cincinnati, November 1975).

III

The delegations determined and coordinated the program of cooperation for 1976 (Appendix III).

The sides will yearly execute exchange of information about the course of the work. The questions of the exchange of results will be decided for each separate case in conformity with the existing agreements between the USA and the USSR in this field.

For the preparation of the forthcoming Symposium "Intensification of Biochemical Methods of Waste Waters Treatment" (USSR, Moscow, May 12-26, 1976), the following was agreed upon:

- each side will present 5-6 reports to the Symposium;
- the sides will exchange the report titles prior to February 1, 1976;
- the texts of the reports shall be exchanged in two copies in Russian and English, prior to April 15, 1976;

Both sides noted that organization work for carrying out the Sumposium "Waste Water Treatment – Physical-Mecahnical Treatment Facilities" to be planned for September 1976 in the USA will be considered in the course of delegations meeting in May 1976.

Paying great attention to increasing the efficiency of cooperation, the delegations consider it advisable to carry out in the future long-term exchange of specialists on various problems of waste water and sludge treatment.

The delegations agreed to carry out a long-term exchange of specialists during 1977:

- of Soviet specialists in the US on the problem of the use of technical oxygen in biological treatment, and
- of American specialists in the USSR on the problems of biological treatment plants' operations.

The detailed exchange program will be agreed five months prior to the date of the participants' departure. This exchange will be carried out on the basis of equal and "receiving-side-pays" basis.

In the course of this visit to the US the Soviet delegation visited water treatment plants in or around the cities of Norfolk, Philadelphia, Harrisburg, and Erie, the Taft Scientific Research Institute and the Cyanamid Company.

Both sides expressed their satisfaction that the meeting was conducted in an atmosphere of friendship and in a spirit of mutual understanding, thus contributing to the further development and strengthening of cooperation in the field of environmental protection.

This protocol was signed on November 21, 1975, in Washington, D.C. in two copies, in English and Russian, both texts being equally authentic.

From the Soviet Side	From the US Side
R. Slavolyubov	Harold P. Cahill, Jr.
Chief of Delegation	Chief of Delegation

APPENDIX I

LIST OF SOVIET PARTICIPANTS

1. R. Slavolyubov	Chief of the Department, GLAVPROMSTROYPROEKT, GOSSTROY, USSR Chairman of the USSR Delegation
2. V. Ponomarev	Head of the Laboratory, VNII VODGEO, GOSSTROY, USSR
3. I. Myasnikov	Head of the Sector, VNII VODGEO GOSSTROY, USSR
4. A. Belevtsev	Senior Researcher, VNII VODGEO GOSSTROY, USSR
5. I. Maksinmenko	Senior Researcher, Interdepartmental Environmental Protection Council of State Committee of Scientific and Technical Affairs
6. M. Levchenko	Deputy Manager, Trust "ORGCHIM" MINCHIMPROM

LIST OF AMERICAN PARTICIPANTS

1. Harold P. Cahill, Jr.	Chairman of the U.S. Delegation, Director Municipal Construction Division, US EPA Washington, D.C.
2. A. Breidenbach	Assistant Administrator for Water and Hazardous Materials, EPA, Washington, D.C.
3. A. Paretti	Consultant, Water Programs, EPA, Washington, D.C.
4. Jesse M. Cohen	U.S. EPA, Cincinatti, Ohio
5. Walter J. Weber	University of Michigan, Ann Arbor, Michigan
6. Russell Culp	Culp, Wesner & Culp, El Dorado Hills, California
7. Robert Polta	Metropolitan Waste Control Commission St. Paul, Minnesota
8. A. Cywin	Director, Effluent Guidelines, EPA Washington, D.C.
9. I. Gellman	NCASI, Pulp and Paper Industry, New York New York
10 R. Dunlap	Carnegie-Mellon University, Pittsburgh, Pa.
11. A. Marek	American Cyanamid, Bound Brook, New Jersey
12. F. Sebastian	ENVIROTECH, Menlo Park, California

APPENDIX II

LIST OF REPORTS PRESENTED AT THE USSR–US SYMPOSIUM "WASTE WATER TREATMENT – PHYSICAL-CHEMICAL TREATMENT FACILITIES"

FROM THE USSR

1. Levchenko, M, N. "Treatment of Waste Water from Chemical Plants"
2. Myasnikov, I.N., Gandurina, L.V., Butzeva, L.N. "Studies on Waste Water Treatment with Flocculants Application"
3. Korshak, V.V., Zubakova, L.B., Gandurina, L.B., "Synthesis of Cationic Polyelectrolytes for Treatment of Natural and Waste Waters"
4. Myasnikov, I.N., Balakin, B.A. "The Removal of Volatile Suspended Solids from Waste Waters"
5. Belevtsev, A.N., Maksinmenko, Yu. L. "Studies on Oxidation Processes of Cianides and Phenols in Waste and Natural Waters by Using Chlorine Dioxide"
6. Panova, V.A., Goriatchev, N.S., Lurie, U.U. "Examination of Oil-Containing Waste Waters Chemical Composition after their Treatment in Aeration Tanks"
7. Ponomarev, V.G., Zakharina, S.B. "Treatment of Concentrated Waste Water Containing Oil Emulsions"

FROM THE US

1. Cohen, Jesse M. "An Overview of Physical-Chemical Treatment"
2. Weber, Walter J. "The Role of Activated Carbon in Physical-Chemical Treatment"
3. Culp, Russell "Design of Facilities for Physical-Treatment of Raw Wastewater"
4. Polta, Robert "The Operation of the Physical-Chemical Treatment Plant at Rosemount, Minnesota"
5. Lacy, William, Cywin, Allen "Physical-Chemical Treatment of Waste Waters from the Petroleum Refining-Petrochemical Industries"
6. Gellman, Isaiah "Current Status and Directions of Development of Physical-Chemical Effluent in the Paper Industry"
7. Dunlap, Robert, McMichael, Francis "Dilemma of Coke Wastewater Disposal"
8. Marek, Anton, Askins, William "Advanced Wastewater Treatment for an Organic Manufacturing Complex"
9. Sebastian, Frank "Cost Benefits of Physical-Chemical Treatment"

APPENDIX III

PROGRAM

USSR-USA COOPERATION OF WORKING GROUP ON PREVENTION OF WATER POLLUTION FROM INDUSTRIAL AND MUNICIPAL SOURCES

No	Title	Form of Work	Responible for		Time	Expected Result
			From the USSR	From the USA		
1	Modernization of existing and development of new combined facilities with high efficiency for wastewater treatment, including hydrocyclones, multistage settlers, flotators, facilities for usage of technical oxygen, investigations of usage of flocculants and coagulants	Joint development of themes, scientific information and specialists delegation exchange Symposium on "Improvement of Biochemical waste water treatment methods" (USSR, May, 1976, 16 days, 7 specialists) Symposium on theme: "Wastewater treatment Physical-Mechanical Treatment Facilities" (USA, September, 1976 16 days, 7 specialists)	VNII VODGEO GOSSTROY USSR	EPA	Through 1978	Improvement of the efficiency of existing and development of new treatment facilities reduction of space for loction, reduction of reagents as cost price of waste water treatment
	Development of hydrocyclones and flotation facilities; scheme of usage of coagulants		VNII VODGEO Gosstroy USSR			
–	Development of tubular and plate settlers and facilities for usage of technical oxygen; scheme of usage of flocculants.	Information and delegation exchange		EPA		
2.	Intensification of wastewater process in petrochemical, chemical, petroleum refining, pulp and paper, and metallurgical industries.	Information and delegation exchange	VNII VODGEO GOSSTROY USSR	EPA	Through 1978	Increasing of wastewater treatment efficiency introduction of new treatment schemes, maximize usage of treated waters in recirculation
–	Intensification of wastewater treatment process in metallurgical and petroluem-refining industries		VNII VODGEO GOSSTROY USSR			
–	Intensification of wastewater treatment process in petrochemical and pulp and paper industries.			EPA		

PROGRAM

USSR-USA COOPERATION OF WORKING GROUP ON PREVENTION OF WATER POLLUTION FROM INDUSTRIAL AND MUNICIPAL SOURCES

No	Title	Form of Work	Responible for		Time	Expected Result
			From the USSR	From the USA		
3.	Development of highly efficient methods and facilities for removal of nutrients and treatment of municipal wastewaters	Joint development of themes, informationand delegation exchange	VNII VODGEO GOSSTROY USSR	EPA	1977	Development of new treatment facilities for prevention of water basin entrophication and development of new treatment systems with the maximum usage of treated water in recirculation at industrial plants.
–	Development of methods and facilities for removal of nutrients and treatment of municipal wastewaters.		VNII VODGEO GOSSTROY USSR			
–	Usage of treated water in recycling systems at industrial plants.			EPA		
4.	Treatment of wastewater sludges.	Information and delegation exchange.				Reduction of cost price of waste water sludge treatment increasing of treatment facilities efficiency.
	Stabilization and dewatering of wastewater sludges		VNII VODGEO GOSSTROY USSR			
	Technology and facilities for utilization and treatment of wastewater sludges.			EPA		
5.	Exchange of two Soviet specialists for 4 months in US on the problems of usage of technical oxygen at biological waste water treatment plants.	Study of research work of American companies and organizations, participation in scientific studies			II Quarter 1977	Studying of the US experience in the field of waste water treatment.
	Exchange of two American specialists for 4 months in the USSR on the problem of biological industrial and municipal waste water treatment plants.	Acquaintance with research work of the Soviet organizations and institutes, participation in scientific studies.			III Quarter 1977	Studying of the USSR experience in the field of waste water treatment.